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THE TECHNOLOGY

OF

IRON ENAMELLING & TINNING

BEING COLLECTED PAPERS

BY

JULIUS GRÜNWALD.

TRANSLATED FROM THE GERMAN BY

HERBERT H. HODGSON,
M.A. (CAMB.), B.SC. (LOND.), PH.D. (HEIDELBERG),
LECTURER AND RESEARCH CHEMIST AT THE MUNICIPAL TECHNICAL COLLEGE, BRADFORD;
LATE MAJOR SCHOLAR OF TRINITY COLLEGE, CAMBRIDGE, AND
BRADFORD CITY COUNCIL TRAVELLING SCHOLAR.

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PREFACE.

From various quarters I have been requested to collect in book form my latest publications upon the enamel and tinning industries, in order that these articles, which are scattered throughout a large number of periodicals and have appeared at different times, may be brought within reach of those fellow-workers who have not access to special literature.

The especially favourable reception accorded to my manual on modern enamel technology, *Theorie und Praxis der Blech- und Guszemailleindustrie*, Leipzig, 1908, which has necessitated English and French editions, leads me to hope that many fellow-workers in our industry have been rendered a service thereby. I heartily wish that the present modest compilation of my technological and historical publications may arouse the same interest and indulgent criticism which my above-mentioned book has received. The choice of title and the collected essays are explained by the fact that the majority of enamel firms also engage in tinning.

The following chapters are the outcome of studies originating in the very restricted leisure time possessed by the director of a large works. His sincere wish has been to render accessible to fellow-workers much observation and experience, while the leading motive of all these publications has been to furnish information and suggestion. At the same time, they should help to remove the anxious aversion to disclosing works' secrets, and cause us to recognise that the enamel industry may only be maintained at its present high level by incessant investigation into the manufacturing processes, and by the suitable utilisation of modern scientific

achievement, these demanding from all their respective literary contribution. The modern trend of our industry and the growing appreciation of the work of technically-trained experts are fortunately building up favourable anticipations for the future development of the enamel industry.

My best thanks are due to my Publishers, Messrs C. Griffin & Co., Ltd., for the care bestowed upon the production of this English edition as a companion book to *Enamelling on Iron and Steel*, which they have made so widely known.

THE AUTHOR.

LAFESCHOTTE, DOUBS.

DR JULIUS GRÜNWALD

CONSULTING ENGINEER TO THE ENAMELLING INDUSTRY, VIENNA, AUSTRIA.

Dr GRÜNWALD is prepared to advise on matters relating to Correction of Defects — Formulæ for Enamels — Organisation of Works — Wages — Methods of Enamelling, Drying and Welding — The Compressed Air Process — Testing and Analysis of Raw Materials — Prices and Supplies of Materials.

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ENAMELLING AND TINNING.

CHAPTER I.

A CONTRIBUTION TO THE HISTORY OF THE ENAMELS AND OF THEIR TECHNOLOGY.[1]

THE covering of bodies, particularly metals, with enamel has long been known. If the present-day enamel be briefly but scientifically designated as a boro-sodium-potassium-aluminium silicate generally coloured by metallic oxides, then the following definition given by Claudius Popelin [2] deserves to be quoted, since this, notwithstanding its length, may be described as most clear and comprehensive : " Enamel is a glass fusible at a low temperature, and usually compounded of a mixture of borates and silicates. This mixture, originally colourless, combines with the greatest ease, with all or almost all metallic oxides, under the influence of a pyrotechnic operation, thereby acquiring various bright or sober colours, according to the nature of the oxide, which the enameller can vary at will and which place a comprehensive palette at his disposal."

The covering of burnt earthenware, porcelain, etc., with an enamel flux took place historically about the period of the discovery of glass. Since the time when man enamelled metals, especially gold, silver, and copper ornaments, he began to be interested in problems connected with artistic enamels.

Coloured enamelled earthenware has been found in the ruins of Thebes. Many buildings also in ancient Egyptian cities exhibit enamelled brickwork.

[1] Appeared in Vol. I. Part II., February 1909, of the *Archiv für die Geschichte der Naturwissenschaften und der Technik*, Leipzig.

[2] Claudius Popelin, *L'art de l'Email*, Tours, 1868.

That the Egyptians knew how to adorn silver vessels with enamel pictures has been recorded by Pliny the elder. From Egypt the enamelling arts were transmitted to Greece and thence to Rome. Brongniart in his classical work, *Traité des arts céramiques*, maintains that the art of enamelling came to Italy via Arabia, Spain, and the Balearic Islands. Through Roman expeditions the art passed into England, France, and Germany. The proofs of the first beginnings of the art in Germany (at the time of the Merovingians), France, and England are numerous. In the Museum at Oxford is an enamelled ornament which was found in Somerset and whose inscription dates to the time of Alfred the Great; there are also specimens of Norman origin.

From the fourth to the eleventh century the chief centre of the art was at Constantinople, from which it was afterwards transferred to Italy, France (Limoges), and Germany (Cologne).

It would be beyond our scope to enter into the details of the methods known for producing enamelled ornaments. These may be briefly summarised as follows:—

In the enamelling arts employed upon the noble metals and copper, the following divisions are distinguished:—

Enamel Cloisonné (**Zellenschmelz**), also characterised as artistic Byzantine enamel. The contours of the design are formed by soldering artistic strips of thin metal on the ornament, the spaces between being filled with the corresponding enamel, fired in the muffle-furnace, and afterwards polished.

Enamel Champlevé or **Grubenschmelz**, typical of the French school (Limoges). Here the contours of the design are produced by excavating cavities in the metal plate, only the outlines of the design in the form of thin partitions being allowed to remain.

"**Email translucide**," or **Italian enamel**, denotes that form of execution in which the contours of the design were usually engraved in silver, the whole object afterwards receiving a thin coat of a coloured transparent enamel. The effect after enamelling differed from place to place according to the varying depth of the engraving.

Finally, the term **enamel-painting**, or "**Email peint**," is still in use for a branch of enamelling in which two periods may be distinguished. The first period is known as that of the "*Old Limoges Style*"[1] of the time of Francis the First (1515–1547).

[1] Later investigations have established the existence of an independent Gallic enamel industry for bronze, especially concerned with the ornamental pins of the La Tène period. See, for example, Wiedmer-Stern, *Das gallische Grabfeld bei Münsingen* (The Gallic Excavation at Münsingen), Bern, 1908, pp. 28 and 88.

The enamel plate, generally made of copper, was covered with a dark (black, blue, or grey) enamel coat. After firing, figures, weaker or stronger according to the relief desired, were put on with white enamel, and the impression of bas-relief thereby brought about. The second period of enamel painting began a generation after the first. This is the so-called period of the "*Miniature Style,*" which was invented about the middle of the sixteenth century by Jean Tontin, a goldsmith of Chateaudun, and brought to an extraordinary state of perfection by the famous miniature painter Jean Petitot (1607–1690).

Varying opinions exist as to the origin of the term "enamel." Labarte recognises the origin of the expression "smaltum" in the brilliant object "haschmal," the account of which is in the visions of Ezekiel. Whether the substance "electron," often quoted by Homer, Hesiodus, and Sophocles, is identical with enamel, has not as yet been unquestionably established.[1] The word "smaltum" is found for the first time in the ninth century, and it lies much nearer the Old High German "smelzan, smaltzan," from which "schmelz" or "schmelzen" is derived.[2]

Even in the eleventh century the term "electron" is used for enamel in a celebrated book by the monk Theophilus.[3]

As the demand for the artistic enamels of antiquity and the Middle Ages increased, so the enamelling of gold and silver gave place to that of copper vessels. In the eighteenth century, if we except the somewhat scattered industry of miniature painting upon boxes, etc., which still was practised and which, strictly regarded, had little affinity with the ancient art, a complete decline of the enamelling art has to be recorded.

This short abstract from the history of the enamel arts, dealing with the forerunners of our present enamel technology, is indispensable, since the progressive transition from the enamelling of gold to that of silver and copper is thereby given, while its extension to iron has now to be taken into account.

To the nineteenth century, the age of the most important of Europe's social, educational, and technical revolutions, was reserved the renaissance of the art of enamelling to a new significance.

[1] In ancient times "electron" had a twofold meaning; originally it stood for ornaments produced from a gold-silver alloy. It appears as if the enamelled vases mentioned by Pliny the elder had a gold-silver alloy as basis. The Emperor Justinian I. (514–527) likewise sent an enamelled vase (*gabatum electrinam*) to Pope Hormisdas (514–523). Here the term "electron" appears in use for the first time as an adjective.

[2] E. Molnier, *L'Émaillerie*, Paris, 1891.

[3] *Diversarum artium schedula* (Treatise on various Arts).

The art of enamelling became the enamel industry. In the age of coal, steam, iron, and steel, what was more suitable for our modern requirements than the application of the half-forgotten art of enamelling to iron utensils?

In the history of the development of our present art of iron enamelling, or more correctly expressed, of the modern industrial technology of iron enamelling, we are able to speak of two periods with regard to the iron materials employed, viz. of the original enamelling of cast iron exclusively, and the later application to sheet steel. Again, both periods are characterised by two kinds of enamel technology, while even a third branch has recently sprung into existence.

The earliest enamelling method with respect to iron was the so-called *dusting-on* (Aufpudern, or Pudern) of the enamel. The carefully cleaned and pickled iron object was heated to redness in the muffle-furnace, and upon it the finely-ground dry enamel[1] was dusted by means of a finely-meshed sieve until the necessary thickness of coating was attained. The enamelled object was again taken to the furnace and the enamel melted. Frequently a so-called "ground-mass" or "ground-enamel" was first laid on. The enamels used in the dusting process, especially when applied to cast iron, must obviously be of relatively low fusibility. This works' method was expensive. In addition, the early direct firing muffle-furnaces were of imperfect construction, while the pickle acids and the raw materials for the enamels, such as borax, soda, saltpetre, and many others, were costly.

The first period began about 1840, and lasted until 1860. About this time the enamelling of sheet-iron ware began to be carried out in Austria and Germany. At this stage only the enamelling of the interior of utensils was understood. The outer surface and the edge were painted black. Originally the enamelled object was fired separately and in a muffle of small dimensions. By means of tongs the object was gradually moved from the cooler zone of the furnace in front to the hotter portion in the rear.

In the year 1851 appeared the first manual on the art of enamelling cast iron by one Moritz Vogelsang of Vieweg in Braunschweig. Notwithstanding the many charming opinions and assertions of this author which at the present time are obsolete, this little volume teems with correctly observed properties of the raw materials. The value of this booklet, which without

[1] See page 7.

question was written by an eminent chemical expert, is manifoldly higher than many works written later. We learn from it that about 1850 the moist enamelling of cast-iron vessels had already been partly adopted.

A comparison of the cost of the most important of the raw enamelling materials of that day with those in use at the present time is most interesting:—

		1850. Mk.	1908. Mk.
100 kg.	Venetian or French borax cost about	190	about 34
„	finely-ground quartz „ „	9	„ 4
„	„ „ felspar „ „	9	„ 5
„	purified clay „ „	4 40	„ 3
„	commercial tin oxide „ „	420	„ 360
„	anhydrous soda „ „	126	„ 12
„	sodium saltpetre „ „	60	„ 29
„	fuming sulphuric acid „ „	60	„ 8–10
„	coal „ „	0 30	„ 2
„	ground-mass „ „	90	„ 25
„	cover-mass „ „	198	„ 55

Note the extraordinary difference in price between borax, saltpetre, and tin oxide. With the discovery of the great boro-sodium calcite supply (Ulexite, $NaCaB_5O_9 6H_2O$) in Peru, and the scientific investigation of the Strassfurt deposits by Franck in 1860, whereby boracite ($2Mg_3B_8O_{15} + MgCl_2$) was isolated in large quantity, it was found possible to obtain considerable amounts of raw material for the manufacture of octahedral borax ($Na_2B_4O_7 10H_2O$). The latter soon supplanted the French or prismatic borax, which was mostly prepared from the boric acid of the Tuscan fumaroles. A similar development has taken place in the case of soda, which, thanks to the ingenious work of Leblanc and Solvay, quickly came upon the market at cheap prices.

While earlier, smalt or zaffers served almost exclusively for the *blue* coloration of enamels, whereby at the most only a blue of variable colour intensity could be prepared (on account of the fluctuating content of cobalt oxide), an important forward step was made with the manufacture of pure cobalt oxide. Since smalt was a cobalt oxide silicate of variable composition, it became necessary to prepare a standard cobalt oxide, and this the Saxon Blue Colour Works succeeded in doing by means of a newly-discovered method of separation. Owing to the above process, the Saxon Blue Colour

Works mentioned have been able to maintain their leading position up to the present time. In like manner the discovery of the *pink* colours, especially of the pink rose (*nelkenfarben*) by Booth in the year 1835, deserves to be recorded as an interesting event in the preparation of coloured enamels.

The second and most important epoch of the technology of iron enamelling was made possible by different causes. In this period the enamelling of cast as well as of wrought iron and sheet steel was made exclusively by the *wet process*; the carefully pickled iron object was coated with finely powdered enamel by the aid of water plus clay additions, the object being afterwards dried and fired in the muffle-furnace.

Special credit must be accorded the German machine industries, which by removing what was regarded as the insuperable expansion difficulty, and by the continual construction of improved presses which to-day are the standard types, as well as of other machines for the working up of steel, have brought about an intimate connection between the manufacture of crude iron wares and the application of enamels to them. It is therefore the business of the machine manufacturer as well as of the enameller to wrestle with any fresh difficulties having their origin in the revolutionary inventions of Bessemer, Thomas, Gilchrist, and Siemens-Martin. New enamels and fresh methods of working had to be invented, in order to discover the correct way of making possible an harmonious union between sheet steel and enamel.

The above period was the difficult time in the history of modern enamel technology. From various quarters different methods were proposed. A leading American firm sought to meet the inconvenience inherent in the changed physical and chemical structure of the basic Siemens-Martin sheet steel employed, by the electrolytic nickeling of the pickled crude wares before enamelling. In France the experiment was made of welding together two iron plates with a steel core, and subsequently rolling them out in order to acquire a sheet of the original species.

That all these expedients did not meet the difficulty is obvious from the extraordinary development of the German and Austrian enamel industry. Rejecting all the inadequate proposals of their competitors, the German enamellers speedily discovered the one and only way, which lay in the preparation of new enamels having suitable physical and chemical properties, especially with regard to expansion coefficient, freedom from lead, absolute innocuousness,

and also durability, thereby establishing the permanent reputation of the German and Austrian enamel wares. The German enamel industry quickly learned how to free itself from the prevailing empiricism which had ruled in the preparation of enamels, as well as in factory management. The scientifically trained chemist supplanted the earlier empirical investigator, and from this time, when science and technique worked hand in hand, dated the extraordinary advance of enamelling technology.

The development of scientific fuel technology must unquestionably be regarded as an additional important factor in the history of scientific enamelling. Fuel technology was based upon the theoretical work of Ferdinand Fischer, Bunte, Orsat, Toldt, Schmatolla, Siemens, etc., who investigated processes of combustion, combustion products, and ventilation problems, as well as gas analysis.

In place of the expensive direct firing of the smelting and muffle-furnaces, came the indirect semi-gas, regenerator-gas, and recuperative firing (Siemens). Where earlier up to 500 kg. of coal per 100 kg. of finished enamelled wares were consumed, now 120 to 150 kg. suffices, according to the quality of the coal and the construction of the muffle furnaces.

We have already dealt with the influence of the specialised German machine industry upon the preparation of large quantities of stamped, pressed, or folded sheet-iron wares for the enamel trade. The unwieldy and primitive beam press was replaced by the friction, eccentric, and recently the hydraulic press. In this speciality German industry has reserved for itself a commanding position. The centres of this important industry for constructing sheet-working machines are Aue and Niederschlema in Saxony, Göppingen in Wurtemberg, Bonn, and Berlin. What was performed earlier by manifold hand labour, such as trimming, folding, etc., is now done by machinery.[1] Here a rich field for invention awaits the machine-maker. Whoever enters a large enamel works at the present time will be astonished at the ingenious mechanical drying shelves, drying stores, transport and pickling equipment.

On the other hand, it appears as though the enamelling process itself will long remain a manual operation exclusively, since the experiments undertaken in several places with the object of

[1] Quite recently the folding of rough wares by means of ingeniously constructed machinery has been successfully replaced by electric welding. *Die Allgemeine Elektrizitäts-Gesellschaft* in Berlin has greatly profited by the above process.

accomplishing the enamelling or "Auftragen" by means of machinery are not by any means satisfactory, although they have afforded interesting results (D. R. P. 134,864).

The advantage, however, of having every single piece of enamelled ware separately enamelled by the hand of a skilled workman is not to be underrated.

A third period in the development of enamelling technology, to be associated with the two previously mentioned, has recently manifested itself, and its results deserve to be recorded as of great promise. The method employed is that of enamelling by means of the finest powdered wet ground-enamel. The latter, made into a fairly consistent mass with water, is ground as fine as possible in the mill, and thrown upon the objects to be enamelled by means of a specially constructed spraying apparatus, worked by compressed air or often carbon dioxide under pressure. By further development on these lines, which in reality is a modern adaptation of the older dusting-on process, a quite appreciable economy in wages may be effected, together with more efficacious enamelling.

A search for the most important dates in the history of the development of this art will prove unsatisfactory, since exact records of any value are not in existence. At the close of 1840 appear the first experiments on the enamelling of sheet iron. Bartelmus in Austria, Gnüchtel in Lauter (1844), Thale in Hartz (1845), Ullrich in Maikammer, (1851) Kerkmann in Ahlen (1863), Gebler in Pirma (1864), Thiel in Lübeck (1867), Haardt in Austria, Wuppermann in Pinneberg and Amberg, and Baumann in Amberg (1872), are among the oldest and most famous names in the history of the enamel industry. At the International Paris Exhibition of 1867 many beautiful enamelled iron utensils from Austria were to be seen. In France sheet-iron wares had early been enamelled by Lalance at the enamel works in Laroche (Doubs). Lalance in the year 1850 established works in America for tinning kitchen utensils, and soon settled there entirely, founding, in partnership with Grosjean, the first American enamel works at Woodhaven in the year 1863, an undertaking which to-day employs over 4000 workers.

The first *drawing-press* for the manufacture of stamped articles, which was very primitive in character, was erected in Belgium[1] in the 50th year of the last century. By the end of 1860 stamping was

[1] From my later researches I find that the first press had already been constructed in France by Adolphe Japy in 1846, and therefore earlier than the Belgian.

already performed in Austria with large spindle-presses without any screw mechanism. At the beginning of 1870, the first modern stamp works with screw presses was erected in Austria by the firm of Haardt & Co. Mönkemöller & Co., of Bonn, appear to have been the first, in the middle of 1870, to erect drawing-presses after the Belgian plan. Some years later we find an improved drawing-press by Schuler of Göppingen in the enamel works of Baumann at Amberg and Zug (Switzerland). The most important machine after the drawing-press is the *planing bench*, whose birth likewise appears to have taken place in Belgium.

While the priority of the first Belgian drawing-press is strong evidence for establishing the origin of *sheet-iron enamelling*, yet, according to the most reliable data at my disposal, the first enamel works appears to have been erected, about the beginning of 1830, by the ancestors of the still existing Bartelmus family at Neu-Joachimstal, near Beraun, in Bohemia, and who engaged in the enamelling of cast-iron objects. The first application of enamel coatings upon sheet-iron utensils occurred in the period 1854–58. The first known works devoted to the enamelling of sheet iron was erected by Bartelmus at Brünn in 1859–60.

At the beginning, the inner enamel was vitreous and grey, and it was only later that the use of tin oxide for making white enamels was discovered. Whereas from earliest times the inner enamelling was performed in the wet way, outer enamels, such as the blue and black varieties, were dusted on by means of tulle bags, the grounded utensil being painted with a very dilute solution of gum arabic to serve as adherent. It was only in 1866–67 that the extension to external enamelling was made.

As for the *muffle-furnace*, the firing was first carried out in cast-iron muffles with basal plates of steel. The first clay muffles were made about 1870–73, to which period also the first attempts at generator-firing may be referred.

The first sheet steel made by Martin's basic process was supplied in Austria by C. T. Petzold & Co.

In about 227 German enamel works[1] over 2500 workers are employed at the present time. The majority of these works lie in Prussia (148), Saxony (38), and Bavaria (23), while among them are about four joint-stock companies and five societies with a limited capital.

The total annual production is estimated at about 1 million dz.

[1] About sixty of these are decorative works.

(2 cwt.) for Germany, of approximate value 70 million marks. The sheet-iron consumption thus rendered necessary is assessed at about 850,000 dz. and 17–20 million marks.[1]

The data for enamelled cast-iron wares are not included in the above, since no statements are to hand. The large amounts of raw materials, chemicals, coal, iron, chamotte, etc., consumed by the enamel industry and which are indirectly to be reckoned, defy, however, an approximate estimation.

Germany exports annually one-third of its enamel production (295,000 dz. in the year 1907). Among the best customers are—

Holland	with	22,700	dz.	in the year	1907
Russia	„	24,100	„	„	„
England and Colonies	„	26,000	„	„	„
Argentina	„	11,000	„		
The United States	„	25,000	„	„	

Immediately behind Germany comes Austria-Hungary with about 47 enamel works (16 in Bohemia, 15 in Mähren, 8 in other provinces, 6 in Hungary), mostly of large dimensions. Its brands count among the oldest and most popular. The number of workers employed in the Austro-Hungarian enamel works may be roundly estimated at 17,000, of which about 3300 are in Hungary. At a great distance behind follow Belgium with about 16 works (mostly in Gosselies), France with about 15 works (Hafeschotte) and over 800 workers, Switzerland with about 12 works (Zug, etc.), Sweden with 8, Norway with 2, North America with about 14, Russia with 8, England and Roumania with 1, Italy with 3, and Spain with 2 works.

For enamelling processes, the endeavour was early to the fore to emancipate the enamel completely from components injurious to health, *e.g.* lead oxide, etc., and to offer the general public a cheap house utensil which was relatively durable and free from hygienic objection. The data quoted in an earlier part of this chapter speak best for the extent to which the enamel industry has grown in so short a time, and that it has not escaped envy in consequence, may readily be understood.

The most absurd and unsubstantiated reports (such as appendicitis being caused by enamel splinters) were circulated broadcast, without, however, injuring in any way the increasing popularity of enamelled wares. It is sufficient to read the refuta-

[1] Dr H. Wuppermann, *Die deutsche Blechemailleindustrie.*

tions of medical authorities such as that of Dr G. Roux on the occasion of the 1899 Medical Congress at Geneva, of Dr Alfred Riche at the Hygienic Congress held at the Paris International Exhibition in 1900, of Drs Dieulafoy and Lucas Championniere of the Paris Medical Academy, and the reports of Dr Vallin, staff surgeon of the French army, in the *Revue d'Hygiène* of 30th April 1901, to be convinced of the weakness of this malevolent calumny. The recent Nobel-Prize holder, Professor Metchnikoff, has shown it to be free from objection on other grounds, since appendicitis is caused by certain bacilli. The Court of Justice at Lüttich, as also a decision of the Barmen Chamber and of the County Court at Elberfeld on 22nd February 1907, severely condemned, under penalty of punishment, the propagation of these reports on the part of malevolent opponents.

At the conclusion of this chapter there still remains to be mentioned the inestimable importance of the industry for utensil enamelling in an economic, and especially in a hygienic sense. By the wholesale manufacture of effective, durable advertisement tablets for different purposes, of inexpensive signs for streets, house numbers, and railway station notices, by the general adoption of clean, cheap spittoons and of other important hygienic conveniences in schools, stations, barracks, etc., and especially in facilitating the cleaning of house and kitchen utensils, the industry here discussed has rendered an undeniable service.

The previous history of modern enamelling technology inspires us with the conviction that by the intimate contact of industry and science, the enamel industry will ever maintain its present enviable position.

CHAPTER II.

THE ECONOMIC SIGNIFICANCE OF THE SHEET-IRON ENAMELLING INDUSTRY.

When, about thirty years ago, the already established enamelling processes for cast-iron wares began to be extended to sheet-iron utensils also, nobody imagined that in a relatively short time this branch of work would be called to play a prominent part of economic significance not to be underestimated.

From modest beginnings, and after inestimable trouble and experiment, the enamelling of house utensils was raised to the rank of being an indispensable necessity. Important factors in the success were not only the energetic far-sighted manufacturers, who spared neither trouble nor expense, but also the epoch-making progress of the iron industry, which provided an ideal material in the soft basic Martin sheet steel for the manufacture of rough wares; the progress in fuel technology, thanks to the brilliant work of Siemens, Sieverts, etc.; the unexampled development of chemical industry which rendered accessible, both in quality and cheapness, raw materials for enamelling purposes such as formerly were almost unknown; and last, but not least, the growing recognition of the necessary co-operation of the chemist and of the intimate connection between science and industry.

That the highly developed technique of machine construction has rendered us important service by placing at our disposal ingeniously contrived machines which facilitate the wholesale production of the necessary cheap and durable rough wares, will be readily acknowledged. What a great advance has been made in the meantime, from the original and small productive dusting-on process to the present rational wet-enamelling methods! Hand in hand with the progressive development of the enamelling industry goes the continuous evolution of adaptable forms for

practical requirements, the production of excellent enamels in every existing shade, and the progressive art of decorative enamelling. This latter, being a development of its older sister the porcelain industry, has endeavoured to vie with it in charm and effect and to capture its secrets.

People who know but little about our manufacture are often heard to speak disdainfully of the present quality of enamels as against older brands. These people, however, are in the wrong, as whatever might be objected against modern enamels, the fact is firmly established that they are in no way inferior to the older specimens. On the contrary, it may be confidently asserted that not only is it understood how to make our modern enamels free from injurious lead compounds, but thanks to our present experience, gained by the investigation of the physical and chemical properties of enamel components and of the enamel itself, there has been brought about a capacity for resistance against chemical and physical agents scarcely known in former times. Complaints as to insufficient durability are only made in individual and very isolated cases, and should be regarded as quite insignificant when the millions of articles annually produced are taken into account. The figures for the small output of twenty-five years ago will well explain the comparative absence of complaint. Unfortunately, our industry has never lacked enemies. The most absurd assumptions and reports have been circulated broadcast by interested competitors, in order to discredit enamelled wares. People have not scrupled to refer the cause of appendicitis to enamel splinters. All these reports, however, have not been able to impede the victorious career of the enamel industry. Hygienic experts of international repute (Lehmann of Würzburg, etc.), who have occupied themselves with the investigation of kitchen utensils for components injurious to health, have to acknowledge the enamelled utensils as being perfectly lead-free. In the latter respect, therefore, we can proudly survey what has been achieved, and have no fear for the stability of the immense progress attained in contrast to the pottery industry, which formerly ruled the market, and which is indissolubly linked with the use of injurious lead glazes.

Owing to its chemical nature and its similarity to glass, enamel will always possess a certain destructibility that is notably peculiar to glass and porcelain wares. In this case, however, the strong iron utensil serves as a nucleus, and often ensures a longer

life to the object. Many who read this will have in their mind's eye dainty foods which have been prepared at one time or another in damaged enamelled vessels. The absence of a small piece of enamel from the utensil, such as may be the case after extended use, has little to do with the excellence of the food prepared therein and with the further use of the vessel. As for the rest, no sensible consumer would try to obtain an unnatural duration of life for an enamelled kitchen utensil; this is unlikely, seeing the great cheapness of the market article, which renders it accessible to the poorest. Moreover, an industry whose lower-priced productions had a more or less unlimited span of life would become quickly paralysed, to the disadvantage of the respective makers, workers, and raw material merchants. In so far as in many cases irrational treatment of the utensils on the part of the housewife comes into the question, such as the heating of empty vessels with subsequent addition of water and similar mistakes, this is being remedied by information and growing experience. On the other hand, a great many utensils now come upon the market able to withstand the most exacting demands possible as to abrupt temperature changes.

The enamel manufacturers have attained a hygienic reputation which is not to be underestimated. The cheapness of the wares has made it possible for people of slender means to purchase clean wash vessels, surgical appliances, etc. The great public bodies, hospitals, schools, and barracks are now able to enjoy the luxury of durable, and thereby economical, washing utensils, slop-pails, etc., all of which are for the preservation of the public health, and therefore to be regarded as indispensable from a hygienic standpoint.

The time we live in is one of advertisement. Great industrial and commercial success is acquired for the most part to-day by means of properly conducted advertising. In this unending competition, what a valuable ally is the enamelled sign-board! In towns, at every corner, and on the walls of large as well as of small shops, artistic advertisements shine upon us in variegated colours, executed for the most part upon enamelled sheet steel, and which, in contrast to all others on paper, wood, etc., remain in excellent condition for many years.

Street numbers, and also the names of stations and places executed upon enamelled sheet steel, facilitate traffic in all directions. Who does not remember the disagreeable impression created

upon the onlooker by the earlier wooden signs on which the letters were painted and varnished, subsequently fading after a short space of time?

Without doubt, the enamelling industry has a still more promising future before it, although we must not lose sight of the fact that export facilities are annually becoming more difficult. The endeavours of separate countries to protect the home industry against foreign imports by means of tariffs daily become greater. Such markets as France, Spain, Italy, Russia, etc., which in the past were excellent for the German and Austrian industry, now lose in importance annually, owing to the origin and growth of enamel industries. For the export of enamelled wares, therefore, only the non-European field holds out the prospect of being accessible for several years to come, with equality of opportunity. Even these conditions yearly become harder, since the entire European surplus production competes, often by cutting prices, for the Asiatic, American, and African markets. The future can only hold in prospect the independence of the non-European countries as regards the enamelling industry. The first beginnings are already in evidence in North America, while South America and Japan will soon follow suit.

After this gloomy review, the outlook upon the future of the home enamelling industry should certainly not occasion discouragement; rather should the facts of the existing export difficulties serve to draw the existing firms nearer together where mutual interests are involved, and to evolve a more economic daily production in order to maintain the important position which our industry occupies to-day. Before proceeding to the erection of additional enamel works, however, too much caution cannot be observed. Unfortunately, too many childish opinions are in existence as to the necessary capital required for the establishing of an efficient modern enamel works with its large equipment and expensive stores of raw material. So much detail is bound up with the construction of an enamel works that few are erected. The times are long since past when one with slender means could establish an efficient enamel works with the prospect of gain. With the present low-selling prices of finished wares only large and comprehensive firms have a chance of existence, unless it be a firm devoted to the production of special classes of goods. Yet in this case also it is well, before going forward, to take advice as to whether a demand exists or not. A modern enamel works requires very considerable

capital and a large bank credit, as the profit fluctuates between 0 and 11 per cent.

Far more important than the founding of new enamel works are the necessary extensions to those already in existence, the union of small and poor firms into companies, the serious combine of the manufacturers for the fixing of common selling prices, and the educating of qualified scientifically-trained experts for the management of the profession. As a defect, it must be noticeable that the large and still developing enamel industry possesses as yet no technical school for the training of qualified overseers and managers, and that a chair for enamel technology does not exist in any of our universities.[1] It is shameful what primitive notions prevail in educated circles as to the nature of enamels and their manufacture. Until quite recently there existed in general no useful technical literature whatever; only in recent years has progress therein been recorded, while some experts assert every obsolete prejudice in defiance of their experience and of scientific investigation. The earlier distrustful trader, with his secrets and also naked empiricism, which have long enough hindered the development of our enamel industry, is yielding by degrees to those of broader outlook, to the great advantage of the industry.

What an important part the industry of enamelling sheet iron plays to-day in a scientific respect may be gathered from the following figures. The average annual output of enamelled iron utensils is estimated for Germany alone at about 90 million kilogrammes, of approximate value 65 million marks, with a sheet-iron consumption of about 90 million kilogrammes, valued at about 20 million marks. In Germany about 25,000 workers are employed, irrespective of the many workers who year by year find employment in the iron works and the chemical industry, and so are directly engaged in the enamel trade by virtue of its consumption of sheet iron and raw materials.

Austria-Hungary occupies the second place, with an approximate annual consumption for Austria of 18–20 million kilogrammes of finished wares, of approximate value 14 million marks, and with a sheet-iron consumption of about 18–20 million kilogrammes, of value about 5 million marks, finding employment for over 7000 workers.

[1] Germany employs about 60,000 workers in the ceramic industry, and possesses for it a national system of excellent specialised schools. Although the German enamelling industry employs almost half this number of workers (25,000), there exists as yet neither special school nor chair. In Austria and elsewhere a similar state of affairs unfortunately prevails.

The Hungarian firms produce 10–11 million kilogrammes, of value about 7 million marks, with a sheet-iron consumption of 9–10 million kilogrammes, in value about 2½ million marks, and employing over 3000 workers.

The French production may be estimated at 10 million kilogrammes, of value 7 million marks, entailing an annual consumption of 10 million killogrammes sheet iron, of value about 2½ million marks, and employing about 3500 workers.

The Belgian output approaches the Austrian in quantity.

The value of the enamelling industry as a customer for the chemical industry may be gathered from the fact that the annual borax consumption by German, Austrian, and Hungarian firms may be estimated at 7 million kilogrammes, tin oxide at ¾ million, soda nearly 3 millions, saltpetre at 1 million, felspar and quartz nearly 12 million kilogrammes. In addition, there is a large consumption of sheet iron, acids for pickling, coal, and similar materials. A certain guarantee for the future development of our industry will be found in the intimate co-operation of science and technics.

CHAPTER III.

A CONTRIBUTION TO THE CHEMICAL TECHNOLOGY OF THE ENAMEL INDUSTRY.

THE chemistry of the industrial enamels now sold on so large a scale is still insufficiently studied. In many quarters enamel has been regarded as of analogous composition to glass. This, however, is only partly true, since a part of the silicic acid in enamels is replaced by boric acid, so that we have to deal with an alkali-alumino-boro-silicate and an alkali-alumino-silicate. The latter in many cases is coloured by dissolved metallic oxides (cobalt oxide for blue, chromium oxide for green, cadmium compounds for yellow, iron oxide for brown, limonite for violet, etc.), or is rendered opaque by the addition of tin oxide, which under certain circumstances remains undissolved (suspended) in the enamel flux.

Generally one works with three varieties of enamel, viz. ground, white, and blue enamels. The following, with certain restrictions, is the basis of all three varieties. The **ground enamel** is one of melting-point 950–1000° C., coloured blue by the addition of about 0·5 per cent. cobalt oxide and 0·2 per cent. manganese peroxide. Its chemical composition should be such that its coefficient of expansion may approximate as nearly as possible to that of sheet iron. In this latter respect the apparently slight addition of cobalt oxide has been found by experience to play a deciding part, and only recently has it been replaced with more or less success by the much cheaper nickel oxide.[1]

White Enamel.—The direct covering of pickled sheet iron with white enamel is excluded, since the tin oxide contained therein not only has an unfavourable influence upon expansion, but also on firing is reduced by the carbon in the iron, forming metallic tin and evolving free carbon dioxide, thereby promoting blister forma-

[1] Julius Grünwald, *Enamelling on Iron and Steel.* Published by Charles Griffin & Co. Ltd., London, 1909.

tion. White enamel is prepared from a mixture of about 25–30 parts borax, 45–60 parts felspar and quartz, 12–18 parts cryolite, 3–6 parts soda, and 2–3 parts saltpetre. To the fused white enamel 8–10 per cent. white clay and 5–10 per cent. tin oxide are added at the mill.

Blue enamel corresponds approximately in composition to white, except that the tin oxide is omitted; the blue colour is acquired by the addition of about 1 per cent. cobalt oxide to the mixture, and the saltpetre is reduced to a minimum.

The specific gravity of the individual enamels was found by me to be as follows:—

Powdered ground enamel, including additions but without water	2·04
Powdered ground enamel, including additions +30 per cent. water	1·55
Powdered white enamel, including additions but without water	2·8
Powdered white enamel, including additions +30 per cent. water	1·8

The early enamels of antiquity for decorating artistic vessels were compounded upon another basis, sodium tetraborate, in particular, being omitted. The ancient Persian enamel, the so-called *engobage*, was a lead enamel which, according to requirements, was coloured green by the addition of copper oxide. The Egyptians prepared a red enamel famous for its beauty by the addition of orange-red iron oxide and aluminium-antimony oxide. The preparation of *lustrous enamels*, by the addition of certain metallic oxides in definite proportions to the enamel, was also known to the Egyptians.

The first enamel to be coloured white by tin oxide was prepared by the Spanish Moors and not, as erroneously supposed, by Lucca della Robia in Italy.

Valuable information concerning these epoch-making achievements, is contained in Piccolpasse's book, which appeared in 1548, and which is to be seen in the South Kensington Museum. Therein may be found the preparation of potassium carbonate by igniting the residues obtained in the alcoholic fermentation of wines (wine deposits rich in potassium hydrogen-tartrate). The Italians termed this product *Marzacot*, and prepared from it the base of their enamels, corresponding to the present substance termed "*matt* (Fritte)" (about 30 parts sand and 10–12 parts potash). Tin oxide

was used in conjunction with lead oxide (1 : 4) as the so-called calcine for the preparation of the white opaque enamel. Iron sesquioxide generally served then, as now, for bringing about red coloration.

It would necessitate trespassing too far at this stage to deal with the original mode of production and employment of those most important raw materials which still find use in the enamel manufacture. The discovery of bismuth in 1529 by Agricola may, however, be mentioned, a substance which according to L. Franchet,[1] had in all probability been already used by Xanto Avella di Revigo (1530 to 1550) for the preparation of lustrous enamel (silver-bismuth lustre). We are indebted also for the discovery of ceramic gilding by means of metallic gold to an Italian, Giacomo Lanfranc by name, from Pesaro (1569), and not, as generally understood, to Antonio Lolli.[2]

This modern manufacture of glasses with beautiful iridescent colours owes its origin to a Hungarian glass works at Zlatno in Hungary, where the process was discovered accidentally in the year 1860, details of which will be related in due course. Lobmeyer in Vienna was the first to work out this process on a practical scale, and his products are regarded even to-day as among the most beautiful of their kind, being in many cases unequalled.

Let us now return to the analytical-technical side of enamels, where the following points remain to be noticed.

The analysis proper of an enamel offers no kind of difficulty, and is similar in essentials to that of glass. It is rendered difficult only by the presence, often in slight quantity, of various metallic oxides, and by the exact determination of the boric acid. Unfortunately in our case chemical analysis does not always afford an exact picture of the raw materials which are mixed together in practice, and the value of the most accurate analysis is often illusory even in the hands of skilled enamel experts, and for the following reasons: Enamels are differentiated according to the components mixed and melted together, *e.g.* soda or potash felspar, borax, soda, cryolite, fluorspar, clay, etc., or quartz, borax, soda, cryolite, clay, or by the partial substitution of quartz for felspar and of boric acid for borax. The analysis certainly gives the exact content in silicic acid, boric acid, alkali and aluminium oxide, but leaves us generally in the dark as to the amounts of silicic acid which are combined in the form of felspar, clay, or quartz, or the

[1] *Etude sur les dépots métalliques.*
[2] E. Molinier, *La Céramique italienne au xvième Siècle.*

division of the boric acid into sodium tetraborate and pure boric acid, or the various fractions of the total alkalies as felspar, soda, saltpetre, potash, and cryolite; and finally it gives no information as to how the total alumina found was distributed in the original enamel recipe in the form of clay, felspar, and cryolite, all of which ought to be shown by an analysis.

Every expert knows from experience that two enamels of the same chemical constitution may exhibit different properties according as we have to deal with a pure felspar enamel or a quartz enamel, or one produced from borax or boric acid. The difference in the properties of enamels having the same chemical composition lies in molecular phenomena. A calculation based upon analysis of the raw materials to be mixed in practice is generally unreliable and valueless, in consequence of the many possible combinations. The carbonic acid of the soda, the fluorine of the cryolite, the nitric acid anhydride of the saltpetre, etc., volatilise in the heat of the smelting furnace and make it difficult to calculate from the analysis how much alkali as carbonate, and how much fluorine as fluorspar or cryolite, are to be added to the mixture. An example may serve to illustrate this point.

The analysis of a white enamel gave the following data :—

$SiO_2 = 35$	$Al_2O_3 = 15$	$Sb_2O_3 = 9{\cdot}2$	$CaO = 3{\cdot}5$
$MgO = 0{\cdot}22$	$Na_2O = 16{\cdot}3$	$K_2O = 3{\cdot}3$	$B_2O_3 = 17{\cdot}32$

Based upon this analysis the two following enamel recipes were calculated, and on being carried out gave enamels exhibiting different behaviour. The possible combinations from the above analysis is by no means exhausted with the two examples taken.

Recipe I.—The enamel was calculated on the basis of the above analysis, assuming that a pure felspar enamel rendered opaque by sodium metantimonate was under discussion :—

Cryst. borax	47·0 kg.
Felspar	46·0 „
Sodium metantimonate . .	11·0 „
Natural cryolite . . .	9·5 „
Soda (calcined) . . .	0·4 „
Clay	4·5 „
Calcspar	6·2 „
Loss on melting . . .	124·6 „
Additions on grinding (clay) .	$5\frac{1}{2}$ per cent.
„ „ (MgO) .	0·22 „

Recipe II., calculated on the basis of the above analysis, with the assumption that a felspar-quartz boric acid enamel rendered opaque by Sb_2O_3:—

Commercial boric acid . .	32·0 kg.
Felspar	44·0 „
Quartz	5·0 „
Natural cryolite . . .	24·0 „
Soda	1·3 „
Antimony oxide . . .	9·2 „
Additions on grinding (clay) .	5 per cent.
„ „ (MgO) .	0·22

The expert has nevertheless to find a commercial enamel based upon analysis, which after many trial experiments approximates in its properties as nearly as possible to the enamel analysed. On the other hand, analysis has great importance in that the contents of silicic acid, tin oxide, boric acid, and cobalt oxide are respectively determined, as well as any additions of forbidden compounds such as those of lead, arsenic, or antimony.

The extraordinary rise of the enamel industry must in some part be attributed to the not unessential circumstance that while yet in infancy, the successful emancipation from additions of even the smallest amounts of injurious *lead* compounds was brought about, in striking contrast to the purely ceramic industry, which relatively has unfortunately achieved but little success. The method most worthy of recommendation for the rapid qualitative investigation of the smallest amounts of lead in an enamel is the following:—A place on the enamelled object to be tested is spotted with pure concentrated nitric acid and then heated until the acid has evaporated. A few drops of distilled water are then sprinkled upon the place, followed by the addition of a few drops of a 10 per cent. solution of potassium iodide. The presence of even a mere trace of lead is sufficient to develop the characteristic yellow colour of lead iodide.

In Germany, the officially prescribed qualitative test is complicated, and involves the repeated washing of the walls of the utensil under investigation with a 4 per cent. solution of acetic acid (about 50 c.c. acetic acid per litre of water), and after concentrating the liquid and then allowing it to cool completely (filtering if necessary), it is tested for lead with sulphuretted hydrogen. This kind of qualitative test for lead is too complicated, apart from the

fact that for the treatment of enamelled spoons and decorated enamelled wares, which, in the case of goblets, cups, etc., may be ornamented with colours containing lead, although the enamel itself may be absolutely lead-free, the method is inexpedient and objectionable. The method described above, and used by me, has proved trustworthy in practice.

The addition of *antimony* compounds to enamel is prohibited in Austria-Hungary and also in Germany, remaining, however, unobjected to in France, Belgium, and America. It may be asserted that in general, the Austrian, Hungarian, and German firms long ago avoided the addition of lead or antimony compounds. Whether, indeed, the small addition of antimony compounds to the enamel melt is actually injurious to health remains an open question, and in my opinion may be denied. In those countries where this addition is allowed and has been practised for ten years, no case has yet been reported of ill-health due to this cause. The use of antimony mostly takes the form of the sparingly soluble sodium metantimonate (D. R. P. 134,774). The fact that in such enamels the antimony addition seldom exceeds 10 per cent., and in an average culinary utensil enamelled white inside the weight of white enamel employed seldom exceeds 60–80 grms. (therefore a maximum of 6–8 grms. alkaline metantimonate), also supports the careful observations I have made during many years' experience. I am well aware that in this particular my opinion is almost isolated. So long, however, as a case of injury to health after eating food prepared from such enamelled utensils cannot be proved, I must hold to my standpoint based upon experience, with the express declaration that the incontestable opaque-producing property of antimony oxide may allow it in many cases (for cheap bulky articles) and within certain limits (maximum $\frac{1}{4}$ of the customary tin oxide addition), to be substituted for tin oxide. Other additions, which are being proposed daily, have not proved trustworthy. Tin oxide has its value for the manufacturer, since it must be employed upon first-class, durable, beautifully white-coloured wares, for in this respect no other oxide can compare with it.

Fortunately science and practice are in entire agreement with respect to the rigorous prohibition against the addition of the easily soluble lead compounds which are such a menace to health. According to Graham-Otte only $\frac{1}{350}$th of the weight of sodium metantimonate dissolves in boiling water. The employment of

pure raw materials is of extraordinary importance in the enamel manufacture, and the regular testing of these is an important part of the chemist's work. The analysis of a felspar shows how far this approaches the ideal composition of—

Alkali	16·5 per cent.
Aluminium oxide . . .	18·0 „
Silicic acid	65·0

thus indicating whether the product is adulterated by the far cheaper quartz.

Further, analysis is the test for the purity of the expensive metallic oxides, for the moisture content of borax (up to 6 per cent. apart from the 47 per cent. water of crystallisation), for the composition of natural cryolite and for its frequent replacement by the so-called artificial cryolite (*i.e.* sodium fluosilicate), and so protects manufacturers against heavy loss.

Owing to the fact that sodium fluosilicate, Na_2SiF_6, at the present time finds varied uses in enamel and glass works, there will next be communicated a simple method for the rapid volumetric estimation of the pure sodium fluosilicate content (which varies with the possible adulteration by the addition of quartz).

A weighed quantity of sodium fluosilicate is dissolved in hot water and titrated against twice normal caustic soda until phenolphthalein is coloured red. The calculation of the pure content is afforded by the following equation :—

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + 2H_2O.$$

The progress of the Austrian, Hungarian, and German enamel firms owes much to the fact that the home chemical industry furnishes faultless products, such as tin oxide, cryolite, etc., which are greatly in demand and highly esteemed in the international professional world. This is quoted with pride by the Austrian and German chemical firms as evidence in general of their sound, conscientious methods of manufacture. Tin oxide in particular is singled out as one of the most necessary of the raw materials for the enamelling industry. The purity of this product essentially contributes to the success of a faultless white enamel. By incomplete oxidation of the metallic tin during the manufacture of tin oxide, discoloration of the white enamel can arise, giving the appearance of dirty black specks upon the finished ware after firing. These specks are none other than unoxidised tin particles.

Bohemian quartz, and as a rule felspar, also the famous Bohemian enamel clays of the Karlsbad-Zettlitz region, rejoice in an undisputed reputation.

Much may still be said concerning the chemistry of enamels and the development which this at present important industrial field owes to the chemical knowledge of the smelting and manufacturing processes, but this must be reserved for a later treatise. Enamelling literature is unfortunately still poor in scientific books such as would make a hitherto purely empirical province accessible to science. This fact is explained by the youth of the modern enamelling industry as well as by the reticence practised until quite recently, and yet the real rise of our industry dates from the day when the teachings of modern chemistry and the co-operation of scientifically trained technologists began to be secured. An industry which in Germany at the present time employs 20,000 workers (Austria-Hungary from 14,000 to 16,000) and exhibits an annual turnover of about 60 million marks, has established its economic importance and its title to existence.

CHAPTER IV.

THE ENAMEL MANUFACTURE AND THE FUNCTION OF CLAY IN THE ENAMEL.

The increasing importance of the enamel industry has also, during the last few years, entailed the more intimate study of enamelling chemistry. By the scientific knowledge which has been steadily accumulated with regard to the mutual relationship between the chemical properties of the raw materials on the one hand, and the chemical-analytical occurrences in the separate phases of the enamel manufacture on the other, we are in the position to-day of being able to recognise and avoid the manifold manufacturing mistakes which were made in earlier days. In place of the earlier empirical tests and experiments has come a systematic study for solving the problem as to the most favourable enamel compositions.

The value of practical experiments should certainly not be underestimated, and the cases are unfortunately still numerous where certain manufacturing results defy theoretical solution, and yet by a combination of experiments become explicable. Here also the scientifically trained expert arrives at results more speedily and correctly than the empiricist.

For understanding the properties and the compounding of a good enamel, an assiduous study of the raw materials is necessary in addition to a rich practical experience. Unfortunately the complex management of our modern enamel works absorbs the activities of the majority of works' chemists, so that important problems of the highest interest, which could be solved in part within the scope of a well-equipped laboratory, remain untouched.

Before I speak upon the importance of clay in the enamel industry, it is necessary to refer to the carelessness which so much prevails in the preparation of enamels.

A good enamel requires the greatest care to be exercised from the instant when the raw materials are selected and mixed to the

moment of real employment (the covering process). In this respect very defective conditions still prevail in many firms. I have in my mind's eye the exemplary equipment of one of the most important enamel works, whose owners rightly rejoice at their extraordinary reputation, which in spite of many competitive efforts has never been surpassed. Their peculiar secret lies in the extraordinary care exercised during the preparation of the enamels; only those brands of felspar and quartz are employed whose chemical analysis approaches as nearly as possible the composition below, viz., for *felspar*:—

SiO_2	64–66 per cent.
Al_2O_3	19–17 ,,
K_2O	14–15 ,,
Fe_2O_3	traces

and for *quartz*[1] at least 98 per cent. SiO_2.

For first-class enamels the purchase of felspar in lumps is recommended, these being heated to redness and ground in special drum mills. The *mixing* of the raw materials should be made in as small portions as possible (about 150 kg.) and as intimate as practicable. Unfortunately, the necessary attention is not always given to this point. It is known, for example, that blue enamels (coloured by cobalt oxide) by prolonged mixing of the raw materials appear a much richer blue; hence the blue colour is not only a function of the amount of the cobalt oxide addition (on an average from 1 to $1\frac{1}{2}$ per cent.) but also of the mixing period.

The mixed raw enamel is placed in the *smelting* furnace. In proportion as the enamel goes into the melt, a separation of the enamel into two layers takes place, viz. an upper, specifically lighter (borax, alkali) and a lower, specifically heavier. By insufficient crooking (stirring) of the molten enamel, substances of varying composition and properties are obtained. These frequent sources of error may also be so familiar as to be of constant occurrence, either perhaps through unreliable workers or inadequate supervision.

The enamel finally arrives at the mill. Here the opportunity recurs, through negligence or too hurried working, of lowering the

[1] When opportune I will deal with the important part played by the size of the grains of felspar and quartz for different kinds of enamels. Felspar for white enamel should be employed in a very finely divided condition. Quartz, which favourably influences the transparency of the enamel, should be ground as coarse as possible, especially for ground enamel.

value of an excellent enamel considerably. The present great compass of many enamel works has entailed lack of room, and therefore the necessity for working up the powdered enamel immediately; yet nothing is more injurious to the beauty and value of an enamel than to employ it when freshly ground. The older an enamel (within certain limits) and the more carefully it is purified, so will it possess greater beauty, increased pliability, and enhanced covering power. Some enamel firms, realising the value of these facts, have equipped special enamel purifiers, and employ as white enamel only such as have stood for at least fourteen days, after *grinding and purifying*, in scrupulously clean wooden vats. I am of opinion, however, that an enamel storage of fourteen days is not absolutely necessary, indeed in many cases impossible, since white enamel in particular should be worked up when three to four days have elapsed after grinding.

In collected form the requirements may be thus set out:—

The manufacture of a good enamel necessitates, in addition to first-class raw materials, a regular and most careful mixing and melting together of these, proportions adapted to the composition of the enamel, great carefulness at the mill, and several days' standing of the powdered enamel before use.

Although clay does not occupy the same dominating position in the enamel as in the cognate ceramic industry, yet its rôle, as an addition to grinding, is of indispensable importance: a moist enamelling without the addition of clay is simply impossible.

It is interesting to determine the amount and the origin of the alumina (Al_2O_3) found in a modern white enamel. The total amount of Al_2O_3 may attain from 10 to 18 per cent. of the enamel when ready for use. An example will best illustrate this point; we will take a white enamel of the following raw composition:—

Borax	62	kg.
Tin oxide	5	„
Felspar	60	„
Cryolite	20	„
Calcined soda	4	„
Saltpetre	3	„
White clay	2·5	„
Burnt magnesia	0·2	„
Fluorspar	0·1	„
	156·8	kg.

To 100 kg. of fused enamel the following additions at the moist grinding are made:—

Purified white enamel clay . . .	7 kg.
Tin oxide	7 „
Burnt magnesia	300 g.

The following is assumed to be the composition of the raw materials used:—

Potash felspar—

$K_2O \cdot Al_2O_3 \cdot 6SiO_2$.

K_2O . . .	=	16·81 per cent.
Al_2O_3 . . .	=	18·19 „
SiO_2 . . .	=	64·83 „

(The possible soda content is neglected.)

Natural cryolite—

($AlF_3 \cdot 3NaF$).

Al = 12·85 per cent.	=	24·27 per cent. Al_2O_3
Na = 33·85 „	=	44·12 „ Na_2O
F = 54·28 „		

As an enamel clay, one of the following composition was selected:—

SiO_2 . . .	=	52·4 per cent.
Al_2O_3 . . .	=	33·5 „
Fe_2O_3 . . .	=	0·8 „
Alkali . . .	=	1·5 „
Loss on heating .	=	10·9 „

The loss on melting which a white enamel suffers in the smelting furnace amounts as a rule from 13 to 20 per cent., in our case 19 per cent., and is chiefly made up of the water of crystallisation from the borax (47·2 per cent.), the loss on heating the soda and saltpetre to redness, and partly the fluorine lost.

I may say here that, according to my observations, fluorine is only partly lost during melting.[1] This contrary view has been put forward in a short publication dealing with the subject from another standpoint. I am in agreement with Vondrácek, who says that on analysing enamels containing fluorine, the fluorine and silicic acid content corresponds to that of the unfused enamel, and that only a part of the fluorine volatilises on melting as SiF_4. Also the beauty of the enamel does not suffer from the presence of fluorine within certain limits; and further, I never discovered, during my

[1] For further information consult the author's *Chem. Technologie der Emaillerohmaterialien.*

many years' practice in the most important European enamel works, that any damage or annoyance to the neighbourhood had been caused by an evolution of fluorine or silicon fluoride during melting.

After the enamel has been fused it is conveyed to the wet mill where the following additions are made:—

Tin oxide	7	per cent.
Purified white enamel clay	7	„
MgO	0·3	„

The analysis of the finished enamel after firing gives:—

B_2O_3	16·13	per cent.
Al_2O_3	14·23	„
Na_2O	15·88	„
K_2O	7·37	„
CaO	0·05	„
SiO_2	31·31	„
SnO_2	9·78	„
MgO	0·5	„
F	5·17	„

I must remark, however, that as an example I have chosen a soft, easily fusible enamel of molecular formula:—

$$\left.\begin{matrix} 0{\cdot}75\ Na_2O \\ 0{\cdot}23\ K_2O \\ 0{\cdot}02\ MgO \end{matrix}\right\} 0{\cdot}45\ Al_2O_3 \left\{\begin{matrix} 0{\cdot}66\ B_2O_3 \\ 0{\cdot}16\ SiO_2 \\ 0{\cdot}9\ F \\ 0{\cdot}2\ SnO_2 \end{matrix}\right.$$

The high proportion of Al_2O_3 found in the above analysis is made up of—

3·45	per cent Al_2O_3	proceeding from cryolite.
7·7	„ „ „ „	felspar.
3·1	„ „ „ „	enamelling clay added on grinding.

Total, 14·25 per cent. Al_2O_3.

Clay, in the form of an addition at the mill to the powdered moist enamel, is simply indispensable to our manufacture. Without a clay addition, the finely ground enamel, containing about 30 per cent. water, would quickly sink to the bottom when manipulated in the enamelling dish, and the actual operation of "enamelling" or "laying-on" rendered impossible. Clay causes the particles of enamel to be held permanently in suspension, and in conjunction with the so-called vehicles make possible the creamy consistence

of the enamel. How far these peculiarities are bound up with the colloidal properties of levigated clay still remains to be investigated.[1]

From the fact that the clay addition frequently amounts to 10 per cent. of the total enamel, follows the importance of a correct choice of enamelling clay, since from 10 per cent. of relatively cheap clay the same weight of enamel will be acquired, *i.e.* 100 kg. enamel + 10 kg. clay added on grinding yield 110 kg. of enamel ready for use. It will therefore be apparent that the price of a good enamel clay should be of secondary consideration, since only the best brands ought to be purchased. At the same time clay affords a simple means of regulating the melting-point of an enamel, whereby at the last instant it may be adapted to the actual temperature conditions of the furnace, since the fusion point of an enamel rises with the increased clay addition.

For cheaper enamels, especially for the so-called primary coating, the clay addition may be increased at the mill to as much as 15 per cent. Naturally the enamel will in consequence part with its great hardness and lustre, but will gain in opacity. Therefore, up to a certain limit, clay contributes to the opacity of the enamel. Further, clay imparts very favourable physical properties with respect to extension and tensile strength: all depends upon the correct choice of clay.

Enamelling clay should not be greasy, and should as far as possible be free from iron oxide and calcium carbonate; as a rule kaolin may not be employed, or only with particular care. The absence of $CaCO_3$ is of special importance. Should the clay be heated to redness before its addition at the mill, the indispensable qualities for our purpose would be lost. Ignited clay is excluded as a grinding addition, since the most important property of clay for us, viz. the holding in suspension of the finely-ground enamel particles in the coating dish, is completely lost with the loss of its water of hydration. In judging an enamelling clay it is necessary to know its content of clay substance, undecomposed felspar and quartz. A rational mechanical analysis will serve this purpose; the amount of possible loss at the temperature of the enamel firing is of importance.

By the addition of kaolin at the mill instead of clay, a shrinkage of the white enamel is brought about in places; the enamel is

[1] See the chapter on clay in the author's *Chem. Technologie der Emaillerohmaterialien.*

then said to *divide*, and the kaolin employed is termed too "short." The difference between kaolin and plastic clay lies in the different properties of the clay substance in kaolin and in clay, especially from a physical point of view. Kaolins and clays have already been treated from the commercial side if not from the enameller's standpoint, and in the following remarks I will only deal with the important differences observed in practice when clay is added on grinding in the form of kaolin. Excellent enamelling clays are found around Coblentz (Vallendar, Neuenahr) and in Wirges, also in Podersam, Rakenitz, and Wildstein in Bohemia. According to my experience, clays with about 51 to 55 per cent. SiO_2, 31 to 34 per cent. Al_2O_3, an iron oxide content under 1 per cent., and with complete absence of $CaCO_3$, appear to be best fitted for enamelling purposes.

I pass on to speak about the preparation of clay before its addition at the enamel mill, and, respecting this, I must observe that much is defective still in many enamel works. The clay should be soaked in clean wooden tubs before its manipulation, and should be allowed to remain there several days with frequent stirring, so as to enable it to pass through a fine sieve. From the clay so prepared, the calculated quantities for separate grinding additions are taken, these, however, having been previously boiled some time with a suitable quantity of water. The clay frequently still retains impurities of an inorganic or organic character: the former are removed by levigation and sieving, the latter by fermentation in wooden tubs,[1] with subsequent boiling of the clay. Should this careful preparation of clay be neglected, defects often manifest themselves in the enamel after firing in the muffle (blisters, coloured stains, etc.). Those enamel firms whose brands count among the best for beauty and stability, devote the care here described to the enamel preparation; the additional expense will richly be repaid by the small percentage of defective goods and the improved quality of the enamels.

For coloured enamels, such as ground and blue enamels, the use of coloured clay (yellow or black) is recommended. The iron oxide content of the latter does not unfavourably influence the colour and quality of such enamels, and, moreover, allows economy to be practised by the use of cheaper coloured clays for the enamels mentioned.

[1] Julius Grünwald, *Theorie und Praxis der Blech- und Guszemailleindustrie*, Leipzig, 1908, p. 36.

CHAPTER V.

PURPLE OF CASSIUS: ITS THEORY AND TECHNOLOGY.

Gold purple, or "purple of Cassius," as it is frequently called after its discoverer Cassius of Leyden (1683), is numbered among the valuable ceramic colouring bodies. It is a well-known fact that the genuine purple-red coloration of glazes, glasses, and enamels may only be produced by gold salts. The excellent red coloration produced by copper, under conditions often difficult to obtain, is greatly inferior to the colour given by gold purple. Also bright violet and rose tints, unaffected by heat, are generally obtained by gold salts, which are only replaced by "pink" for certain cheap glazes and enamels. The constitution of the latter, which is prepared from tin oxide, chalk, quartz, and potassium chromate, has received little attention and requires further investigation.[1] In order to study the nature of gold purple, it is necessary to consider the recipes proposed by different experts for obtaining this substance, and also the theories put forward by these inventors to explain the compound formed. The older theories all inform us, in a latent way, how far the chemico-physical phenomena had been foreseen in earlier times, without a precise modern dressing having been imparted to them. The modern physico-chemical ideas, which when evoked have thrown light upon many a hitherto inexplicable chemical occurrence, might also solve this particular problem satisfactorily. Here the researches of an Austrian investigator, Professor Zsigmondy, in Göttingen, may be mentioned, particularly his meritorious work upon colloidal metals.

If a rod of metallic tin be dipped into a dilute solution of gold chloride, the formation of a thick brown-red precipitate is observed after a short time. The colour is still more beautiful if a diluted solution of a tin salt be added in place of metallic tin. Berzelius

[1] See L. Petrik, "Über die Konstitution der Pinkfarbkörper," *Sprechsaal*, 1907, p. 361.

supposed this purple-coloured precipitate to be a compound of $SnO_2 + Au_2O$, viz. 28·2 per cent. Au to 64 per cent. Sn. Earlier it had been found empirically that the precipitate acquired a more beautiful colour the more dilute the solutions of gold and tin salt, *i.e.*, as we shall see later, the more dilute the electrolytes. For tin salt solutions stannous chloride, $SnCl_2$, is employed, being prepared by dissolving pure tin in hydrochloric acid, keeping the tin in excess, and avoiding, as far as possible, the presence of air and heat.

For the better understanding of the problem some of the recipes investigated for the preparation of the purple may be here communicated:—

P. Robert uses aqua regia, consisting of 4 parts HNO_3 (36° Bé.) and 1 part HCl. In 35·59 g. of this aqua regia so prepared, he dissolves 0·63 g. of fine ducat gold. In a second vessel he dissolves 3·19 g. of chemically pure tin in 22·94 g. of the same aqua regia, and adds an equal volume of water. After complete solution, he dilutes once more with the same quantity of water (distilled water whenever possible), filters, and mixes with it the still further diluted gold chloride solution prepared above.

One of the best processes is that of P. Boley. Ammonium chlorostannate or pink salt ($SnCl_4 . 2HN_4Cl$) is prepared by separately dissolving 107 g. NH_4Cl and 350 g. bichloride of tin oxide hydrate ($SnCl_4 + 5H_2O$) in as little water as possible, or 10 g. anhydrous pink salt (70·8 per cent. $SnCl_4 + 29·2$ per cent. NH_4Cl) are taken, 1·07 g. metallic tin added, warmed with addition of 40 g. distilled water until all the tin is dissolved, and then a further 140 g. of water added. In another vessel the gold solution is prepared by dissolving 1·34 g. gold in aqua regia and diluting this with 480 g. water. Both solutions are united and the precipitated gold purple filtered, washed, and dried (moderately). The composition of gold purple fluctuates, the gold content being able to vary between 28 per cent. and 40 per cent.

The Porcelain Factory at Sèvres[1] prepares gold purple as follows:—

The aqua regia consists of 10·200 g. HNO_3 (36° Bé.) and 16·800 g. HCl. Into 18 g. of such an acid is dissolved 1 g. of fine gold, and the whole filtered and diluted with 28 l. water. Then 36 g. of the above aqua regia are taken, and in warm weather 10 g., in cold 6 g. of distilled water poured into it, and the whole cooled by being placed in a water basin. Into this vessel 6 g. of finely-

[1] Hermann, *Die Glas-, Porzellan- und Emaillemalerei*, p. 47.

rasped Malacca tin are thrown, whereby slow but complete solution ensues. This is filtered and the solution poured, with stirring, into the gold solution. During the course of an hour the purple settles completely, and is then decanted and washed with hot water.

Fuchs of Munich adds a solution of $FeCl_3$ to one of $SnCl_2$ until the stannous chloride solution exhibits a green cast. It is then diluted with water and united with the diluted gold solution. The precipitate is treated as usual. C. F. Capaun proceeds in a similar manner.

A trustworthy method for the preparation of purple is as follows[1]:—5 g. $AuCl_3$ are dissolved without acid excess in 10 l. water and mixed with 7·5 g. $SnCl_4$ solution of specific gravity 1·7, accompanied by constant stirring. From the clear brownish-red solution obtained, the purple is precipitated after the addition of a few drops of H_2SO_4. Further treatment is as usual, only in many cases an addition of 0·5 g. Ag_2CO_3 is made to this purple.

Analyses of some varieties of Gold Purple.[2]

Gold Purple.	Gold.	Stannic Acid.	Water.	Analysed by
Beautiful without water .	24·00	76·00	0·00	Proust
Beautiful . . .	79·40	20·60	0 00	Oberkampf
Violet without water .	40·00	60·00	0·00	Oberkampf
Beautiful without water .	28·50	65·90	0 00	Buisson
Beautiful . . .	28·35	64·00	7·65	Berzelius
Beautiful . . .	19·00	Not weighed	...	Fuchs
Dried and brown . .	21·00	Not weighed	0·00	Bolley

It has been found recently that it is advisable to employ sodium gold chloride, $NaAuCl_4$, instead of $AuCl_3$ in solution. The former is obtained by dissolving 1 g. gold in aqua regia, adding 0·2 g. NaCl, and evaporating the solution to dryness on the water-bath.

If we turn again to the real problem of the nature of purple of Cassius, we shall find that contradictory opinions have in turn held the field, especially in earlier years. It appeared as if the chemical composition of the purple might differ according to the mode of its preparation. Macquer[3] made the observation that the colour of gold purple is darker the greater the gold content, and concluded that the substance was a *mixture* of gold and hydrated tin-oxide. Proust found that gold purple, while still moist, is

[1] Tenax, *Die Steingut- und Porzellanfabrikation*, p. 207.
[2] Hermann, *Die Glas-, Porzellan- und Emaillemalerei*. p. 47.
[3] *Comptes Rendus*, lxxv., Oct. 1872, p. 1025.

soluble in ammonia, and on trituration with mercury yields no gold. This fact, therefore, tells against Macquer's view that gold may be found in the purple in a finely-divided metallic state, *i.e.* the purple is merely a mixture of gold and hydrated tin-oxide. It was next assumed that the purple was an oxy-salt, viz. a double salt of stannous and aurous stannates, and that this double salt contains sufficient oxygen to transform the stannous into stannic oxide.

H. Debray, however, appears to have been the first to approach the correct definition of gold purple in terms of the chemical theory which prevailed in his day. His results[1] received apparent confirmation at the hands of later investigators. Debray concluded that gold purple was a lake of stannic and metastannic acids coloured by very finely divided gold, whereby the colouring constituent of the lake, viz. the gold, has been rendered insoluble in its usual solvent, mercury, just as in the ordinary dyeing process, where the fast colours resist the solvent action of water in consequence of their union with the fibre. The following experiment supported Debray's theory:—

A solution of tin chloride is boiled with one of sodium acetate whereby SnO_2 is precipitated. To the solution some $AuCl_3$ is added and then potassium oxalate. The reduction of the gold chloride occurs instantly, with the formation of gold purple. In this case the oxide and the colouring matter (tin oxide and gold) are simultaneously precipitated.

Debray expressed the following opinion with regard to the solubility of this lake in ammonia:—"It is a well-known fact that at ordinary temperatures tin oxide is soluble in ammonia so long as it remains in the moist condition, but loses this solubility under various influences, *e.g.* higher temperature, but especially on drying: these are the same influences which also render gold purple insoluble. In addition, it is well to notice that a solution of gold purple always appears turbid in transmitted light and slowly precipitates metallic gold, while tin oxide remains almost completely dissolved. These known facts appear quite natural if gold purple be regarded as a lake: on the other hand, it is very difficult to explain if the gold is present as oxide in the purple, since more or less complex products are always formed by the action of ammonia upon oxides of the noble metals, although the metal is never in these circumstances set at liberty." By further researches it was found that a similar coloration appeared when water held

[1] *Dingler's Polyt. Journal*, 1870, lxxxiii. p. 292.

alumina in suspension, and therefore on analogy, when tin salts are added to a gold chloride solution. For the above purpose gelatinous alumina was mixed with a gold chloride solution, saturated with sodium acetate, then heated, and a small quantity of potassium oxalate added, when reduction of the gold chloride ensued with formation of the purple.

This gold purple [1] is commonly termed *gold lake* in the ceramic industry, and finds employment in many directions. As it contains no tin, it may be preserved for a long time in the dry state, and is very suitable for transparent glazes. According to Müller the lake is prepared as follows:—92·5 g. alum are dissolved in 2½ l. distilled water, 1 g. gold added as gold chloride, and 50 c.c. glycerine. Then a solution is added consisting of 115 g. dry Na_2CO_3 in 1250 g. distilled water. The carbonate brings about a copious precipitate of alumina. This is heated to boiling, air being allowed to pass through in order to obtain the alumina finely divided in the liquid. As soon as the purple colour has developed, the process is interrupted, and the precipitate washed until the disappearance of the excess of soda solution.

Franchet himself recommends the following procedure:—100 g. of finely powdered kaolin are freely suspended in water and filtered through a hair-sieve (No. 250); it is then boiled, 1 g. gold added in the form of sodium gold chloride ($NaAuCl_4$), and then 110 c.c. glycerine. After some minutes of vigorous shaking a greenish shade appears, which quickly becomes rose-violet. The shaking is now stopped, the whole washed by decantation until the complete removal of the glycerine, and allowed to dry. This gold purple, however, must be carefully protected from light. If the gold lake as here obtained be shaken with mercury, it neither loses its purple colour nor furnishes any gold. Concerning the peculiarity which this lake exhibits of dissolving in ammonia when in the moist condition, the explanation given is as follows:—At ordinary temperature it is well known that precipitated tin oxide, so long as it remains moist, is soluble in ammonia. Dried tin oxide, however, or an oxide of tin obtained by the calcination of metallic tin, possesses this property no longer. These facts might connect the as yet insufficiently explained relationship between the formation and properties of stannic and metastannic acids.

Mercadien, while testing the noble metals, observed similar

[1] Louis Franchet, *Revue des Matériaux de Construction et de Trav.*, published April 1908, No. 36, pp. 92–97.

substances to gold purple (*Probierer purpur*) when a small mixture of tin and gold containing silver was dissolved in nitric acid. Since gold is not dissolved by nitric acid, Mercadien argued that metallic gold, present in a finely divided state, gives the purple colour to the solution. This opinion was also shared by Gay-Lussac, yet the purple so obtained was insoluble in ammonia, and therefore points to the probability that here not an identical but an isomeric gold purple was under examination.

The distinction between the two species of purple (purple of Cassius and Probierer purple) appears to lie in the different modes of forming the tin oxide in each process, since, as already mentioned, the tin oxide obtained by the oxidation of tin at a high temperature is insoluble in ammonia, like its lake. If, however, an alloy of Ag, Au, and Sn be treated with HNO_3 at a gentle heat, a purple colour soluble in ammonia is obtained. Debray[1] established that the SnO_2 in process of formation is soluble in ammonia. Finally, the extraordinarily interesting experiment of Moissan[2] some years ago appears to confirm the view of Debray expressed thirty years previously. Henri Moissan made some experiments with the object of distilling, *i.e.* volatilising, gold in the electric furnace. This proved a more difficult task than with copper[3] and silver, especially if the evaporation were carried out under ordinary pressure. Moissan showed that almost every element may be evaporated in the electric furnace (*e.g.*, for Cu, Moissan employed an arc of 300 ampères at 110 volts, and evaporated about 230 g. in eight minutes). Kahlbaum and Kraft succeeded in distilling gold when at a red heat by using a vacuum under 1 mm. Already in 1802 Robert Hare had obtained success by means of an oxyhydrogen flame. Moissan, however, was able to distil gold rapidly and in greater amounts, thanks to the great heat of his electric furnace. He performed the same experiments with a gold-copper alloy on the one hand, and a gold-tin alloy on the other; he found thereby that copper and tin distil more rapidly than gold, and that a purple-coloured powder forms in the furnace, giving rise to a new purple of Cassius, viz. a CaO purple coloured by gold vapour. Moissan was able to produce different varieties of gold purple according as he brought the gold for vaporisation to his furnace in the presence of aluminium, magnesium, and zirconium oxides, or silica.

[1] *Sitzungsberichte der Académie des Sciences*, Paris, 1879.
[2] *Bulletin de la Soc. Chem.*, April 1906, p. 267.
[3] *Ref. Zeitschrift f. Elektrochemie*, 12 (1906), 434.

Several facts follow from all the hitherto published older and later views, viz. that the gold in gold purple is certainly contained in a finely-divided metallic condition; further, that the purple precipitation is more beautiful according as the dilution of the solutions employed increases (entirely pure water presumed), and finally, that the gold under certain conditions is fixed on other bodies such as tin oxide.

I will now try to explain the formation of purple of Cassius, first on the ionic hypothesis and the theory of colloidal metallic solutions, next upon some other well-known theories. The colloidal solution of stannic acid is very sensitive. The hydrosol of stannic acid is transformed on heating into that of metastannic acid; both hydrosols are converted into hydrogels by small quantities of electrolytes. Colloidal solutions of metals such as gold may be obtained by two processes, either by the reduction of dilute solutions of metallic salts[1] or by Bredig's method of pulverising the metals concerned by the electric arc under water, the metals serving as electrodes. Already in 1857 Faraday, employing the first method, had produced a colloidal ruby-red gold solution by reducing a strongly diluted gold chloride solution with yellow phosphorus. Zsigmondy mixed the diluted solution of gold chloride with 2–4 c.c. of a 0·2 normal solution of potassium carbonate, using freshly distilled formaldehyde as reducing agent. The purity of the water is very important, *i.e.* the greater or less content of colloids therein. The work of Siedentopf, who by employing a microscope (Zsigmondy terms it "ultramicroscope") perpendicular to whose optic axis a powerful conical beam of arc-light or sunlight is sent into the colloidal solution by a lens arrangement, not only demonstrated that the colloidal nature of the gold solutions may be traced to finely-divided gold, but that this phenomenon, in a certain sense also, contributes towards the purple colour of ruby glass. Genuine ruby glass is prepared by adding gold chloride to the glass mass. On slowly cooling, a beautiful ruby-red glass is produced whose gold content only amounts to 0·05–0·06 per cent. Siedentopf and Zsigmondy easily recognised the gold particles therein by the ultramicroscope.

Small amounts[2] of electrolytes act as precipitants towards colloidal solutions. Colloids, similar to solid particles, wander in the electric current, colloidal metals as a rule travelling towards

[1] Zsigmondy, *Zur Kenntnis der Kolloide*, Jena, 1905.
[2] Arndt, *Techn. Anwendg. d. Physik. Chemie*, 1907, p. 264.

the anode. The addition of ions possessing a contrary charge to that on the colloid particles will tend to cause precipitation: a negatively charged colloid will therefore be coagulated by positive ions. The amount of a neutral salt which just brings about precipitation is (reckoned in molecules) smaller the greater the valency of the precipitating ion. The precipitating power is proportional to the square root of the valency of the ion; a divalent has therefore about $\sqrt{2} = 1{\cdot}6$ times as great a precipitating capacity as a monovalent ion, *e.g.* the Sn ion in stannous chloride. Oppositely charged hydrosols precipitate each other, *e.g.* colloidal solutions of gold and stannic acid. On the above theory our problem becomes one for modern physical chemistry to solve. Gold chloride, and also stannous chloride when in solution, are to be regarded as precipitating hydrosols charged oppositely to each other. Purple of Cassius is therefore supposed to be a mixture of finely-divided gold, produced by reduction, and the hydrogel of stannic acid. Zsigmondy found that according to the relative amounts of both colloids taken (gold chloride and stannous chloride), he could prepare varieties of purple richer and poorer in gold, whose colour ranged from dark red to rose.

Whereas in other cases of precipitating red colloidal gold solutions by means of electrolytes a blue colour appears, this is not the case when colloidal stannic acid is present. When we take into account the powerful reducing action of stannous chloride solution, we are able to assume that it reduces the gold chloride to gold, itself being thereby transformed into stannic chloride. Possibly the oxygen of the air has also an oxidising effect upon the stannous chloride, with a primary transformation of a portion into stannic chloride. The stannic chloride formed then reacts with water at ordinary temperatures to form metastannic acid and hydrochloric acid: $SnCl_4 + 3H_2O = SnO(OH)_2 + 4HCl$. The hydrochloric acid formed may possibly act as an electrolyte, thereby promoting the precipitation of the colloidal gold in the purple of Cassius.

Briefly summing up, we are able to explain the formation of gold purple of Cassius, from a purely chemical standpoint and on existing chemical theory, as a colour lake of stannic acid, or of alumina, etc., produced by the reduction of gold chloride to gold (in an extraordinarily fine state of division). From the physico-chemical point of view this purple would be defined as an hydrogel of stannic acid coloured by colloidal gold.

CHAPTER VI.

THE EXAMINATION OF CAST-IRON ENAMELS.

ALTHOUGH the manufacture of enamelled cast-iron utensils is inferior in importance to the sheet-enamelling trade, yet the demand for enamelled cast-iron objects such as baths, kitchen sinks, pipes, siphons, and kettles in particular, also apparatus for the chemical industry, is always an important one, and is in some respects on the increase. The treatment of the cast iron to be enamelled deviates somewhat from that of sheet iron, chiefly with respect to pickling, enamelling, and firing. I have discussed these processes in another publication,[1] and here I will examine the deviations in chemical constitution of enamels for cast iron from those employed for sheet iron.

The enamelling of cast iron is an older process than that of sheet iron,[2] and the earliest record of cast-iron enamelling is by one Bartelmus, about 1836, at Neu-Joachimstat, near Beraun, in Bohemia. Two processes usually come under consideration in the enamelling of cast-iron utensils, viz. the direct dusting on of the cover enamel upon the cast-iron surface heated to redness, or the moist enamelling process where a ground and a cover enamel are used.

Direct moist enamelling with a cover enamel is not as a rule carried out, since tin oxide, which is an indispensable means for producing white opacity in a white enamel (6 per cent. to 25 per cent.), would be reduced to tin by the iron carbon, and the finished enamelled ware would show an ugly surface, blistered by the carbonic acid developed during the tin-oxide reduction. Proposals have been put forward from different quarters for enabling cast iron to be enamelled without necessitating a ground

[1] *Stahl und Eisen*, 27th Jan. 1909, p. 137; further, compare the author's *Theorie und Praxis der Blech- und Guszemailleindustry*, Leipzig, 1908.

[2] See the author's "Geschichte de Emaille und der Emailliertechnik" in the *Archiv für Geschichte der Naturwissenschaften und der Technik*, Leipzig, Feb. 1909.

enamel. The proposals depend upon making the oxidation of the carbon impossible, or very difficult, by a suitable treatment of the iron surface. R. Vondracek,[1] who has published an interesting work regarding this difficulty, and also J. Schlemmer,[2] have both succeeded in obtaining remarkable results; the former covers the cast-iron object to be enamelled with a thinly liquid paste of colcotar (using water weakly acidulated with nitric acid) and heats until solid in the muffle-furnace. By the primary oxidation of the surface there is formed an exceedingly stable union of the cover enamel with the iron. Some American firms appear to have achieved pronounced success by similar methods. Another process[3] depends upon the influence of carbonic acid on cast iron at the heat of the muffle-furnace. The cast iron is coated before heating with a mixture of silicates and substances evolving carbonic acid, such as sodium bicarbonate.

In Europe, however, the above process has been viewed with scepticism, and in actual practice most firms employ one of the two processes referred to at the beginning, viz. either dusting upon the red-hot iron surface an easily fusible enamel, which as a rule contains much lead, or by moist enamelling with the aid of an intermediate enamel known as the ground enamel or ground-mass.

The dusting-on process, which yields excellent results, is restricted, however, to certain objects in consequence of the lead content in the enamel used, and in European firms is only employed for furnace enamelling, etc. Later I will give an example of a white enamel for dusting on, which may be compounded without the addition of lead. The dusting-on process is, however, expensive, while, consonant with their nature, the easily fusible powder enamels are not very stable to acids.

Moist Enamelling.—The process most employed is that of the moist enamelling of the cast iron with the aid of a *ground-mass*. The ground-mass, in contrast to the ground enamel used in the enamelling of sheet iron, is a matt composed, as a rule, of a varying mixture of silicates, silica, borax, and clay. The mass is finely powdered, mixed, and heated in the muffle-furnace in vessels smeared with clay, until sintering begins, *i.e.* until the moment when the water of crystallisation of the borax is expelled and the small quantities of carbonate unavoidably present are decomposed.

[1] *Chemiker-Zeitung*, 13th June 1906, p. 375.
[2] *Stahl und Eisen*, 15th March 1906, p. 350.
[3] D.R.P. 5239 of 22nd April 1879.

Naturally, a too powerful heating of the furnace mass as well as an insufficient period of heating are to be avoided. A good ground-mass should exhibit a white, porous appearance, while the cast-iron utensil enamelled with it should furnish no particles when scratched with the finger nail.

Now that I have discussed the various processes, I will pass on to the study of some current ground-mass recipes, dealing with their chemical composition and the relation of the individual components to the enamel.

I. GROUND ENAMEL OR GROUND-MASS.

1. A ground-mass containing lead, and much employed in earlier times, was compounded of—

Furnace-mass:

Quartz	22 kg.
Borax	13 „
Red lead	4 „
	39 kg.

At the mill, to 20 kg. of the furnace-mass were added—

Quartz	12 kg.
Clay	3 „

The smelting loss of the mass = 15 per cent.

The analysis of the ground-mass when ready gave:—

SiO_2	78·10 per cent.
B_2O_3	8·48 „
Na_2O	3·70 „
PbO	6·88 „
Al_2O_3	2·74 „
K_2O	0·18 „
	100·00 per cent.

Accordingly the molecular formula corresponding to the analysis runs:—

$$\left.\begin{matrix} PbO & 0{\cdot}33 \\ Na_2O & 0{\cdot}65 \\ K_2O & 0{\cdot}02 \end{matrix}\right\} Al_2O_3 \quad 0{\cdot}28 \left\{\begin{matrix} SiO_2 & 14{\cdot}20 \\ B_2O_3 & 1{\cdot}30 \end{matrix}\right.$$

2. The following is a recipe of another lead-containing composition:—

Quartz	30 kg.
Borax	16·5 „
Lead carbonate	3 „
	49·5 kg.

To 1 kg. of the matted furnace-mass were added at the mill:—

Quartz	9 kg.
Clay	9 „
Magnesia	0·75 „

Loss on smelting = 16·7 per cent.

The analysis gave:—

SiO_2	74·42 per cent.
B_2O_3	10·34 „
Na_2O	4·58 „
Al_2O_3	4·78 „
K_2O	0·32 „
MgO	1·18 „
CaO	0·08 „
PbO	4·30 „
	100·00 per cent.

The molecular formula is:—

$$\left.\begin{matrix} PbO & 0{\cdot}12 \\ Na_2O & 0{\cdot}47 \\ K_2O & 0{\cdot}10 \\ CaO & 0{\cdot}05 \\ MgO & 0{\cdot}18 \end{matrix}\right\} Al_2O_3 \quad 0{\cdot}3 \quad \left\{\begin{matrix} SiO_2 & 7{\cdot}90 \\ B_2O_3 & 0{\cdot}95 \end{matrix}\right.$$

3. A lead-free mixture which is often employed consists of—

Furnace-mass:

Quartz	10 kg.
Borax	4 „
Fluorspar	0·5 „
	14·5 kg.

Grinding additions to 16·5 kg. of the furnace mass:—

Quartz	5·5 kg.
Clay	5 „

Smelting loss = 11 per cent.

The analysis gives:—

SiO_2	80·80 per cent.
B_2O_3	5·75 „
Na_2O	2·60 „
Al_2O_3	2·44 „
K_2O	0·16 „
CaO	1·86 „
F_2	6·39 „
	100·00 per cent.

Or:—

Na_2O	0·540	Al_2O_3	0·316	SiO_2	17·362
K_2O	0·026			B_2O_3	1·645
CaO	0·434			F_2	4·408

Furnace-mass:—

Quartz	30 kg.
Felspar	30 „
Borax	25 „
	85 kg.

Grinding additions to 73 kg. of the furnace-mass:—

Clay	10·75 kg.
Magnesia	0·8 „

Smelting loss = 14 per cent.

The analysis gives:—

SiO_2	65·72 per cent.
B_2O_3	10·36 „
Na_2O	4·59 „
Al_2O_3	12·00 „
K_2O	6·14 „
MgO	1·05 „
CaO	0·13 „
	100·00 per cent.

Or:—

Na_2O	0·476	Al_2O_3	0·654	Si_2O	6·485
K_2O	0·357			B_2O_3	0·880
CaO	0·012				
MgO	0·155				

For judging an enamel, I place especial value upon the proportion of boric acid to silica and also to the total alkali and lead oxide. In this respect the molecular constitution of an enamel conveys more to the practical man than the percentage by weight. If a comparison be made of the previous four types of ground enamels for cast iron which are most in use, the following conclusions may be drawn:—

The ratio $B_2O_3 : SiO_2$: total alkali and lead oxide is in the examples:—

(1) 1 : 9 : 1·2.
(2) 1 : 7·2 : 0·9.
(3) 1 : 14 : 1·6.
(4) 1 : 6·3 : 1·03.

The average ratio, therefore, of $B_2O_3 : SiO_2 : \Sigma$ alkali + lead oxide = 1 : 9·1 : 1·2.

5. The average composition of a cast-iron ground enamel (containing lead) may be taken as follows:—

SiO_2	74·76 per cent.
B_2O_3	8·74 „
Na_2O	3·86 „
PbO	2·82 „
Al_2O_3	5·30 „
K_2O	1·72 „
CaO	0·60 „
MgO	0·60 „
F_2	1·60 „
	100·00 per cent.

The molecular formula corresponding to the above average composition is accordingly:—

$$\left.\begin{matrix} PbO & 0{\cdot}104 \\ Na_2O & 0{\cdot}521 \\ K_2O & 0{\cdot}156 \\ CaO & 0{\cdot}087 \\ MgO & 0{\cdot}132 \end{matrix}\right\} Al_2O_3 \quad 0{\cdot}372 \left\{\begin{matrix} SiO_2 & 10{\cdot}775 \\ B_2O_3 & 1{\cdot}086 \\ F_2 & 0{\cdot}695 \end{matrix}\right.$$

The lead oxide may here be suitably replaced by the equivalent amount of borax or alkali.

Accordingly the ground-mass is usually prepared as a matt (*Fritte*) containing about 74 per cent. silica, 8 to 9 per cent. boric acid, 4 to 6 per cent. alkali (without lead), and 5 to 6 per cent. alumina. Tin oxide and also cryolite must not be employed as ingredients of this ground-mass.

II. COVER ENAMEL FOR CAST IRON.

As previously mentioned, the cover enamel may be dusted direct upon the red-hot iron with the exclusion of a ground enamel, or it may be laid on moist where the surface has been previously enamelled with a ground-mass.

(*a*) The dusting-on process finds its greatest application in America; in Europe it is usually employed for enamelling furnaces, baths, imitation majolica, etc. This process generally requires an easily fusible enamel having a high lead-oxide content. A lead-free enamel such as No. 7 may, however, be employed with success. Fr. H. Riddle[1] has issued a report upon the composition and properties of the American powder enamels which contain lead. Such an enamel should melt from about 900° to 950° C., and should spread out uniformly and quickly, when dusted on the surface, before the carbon in the iron has the opportunity to be oxidised. The enamel layer in the powdering process is as a rule two to three times as thick as in the case of moist enamelling, thus helping to prevent the evolution of carbonic acid and the accompanying formation of ugly blisters. Enamelled cast iron cools relatively rapidly, and the composition of the enamel must therefore be such that movement may readily take place. A temperature exceeding 1000° C. must be absolutely avoided, otherwise the cast iron will undergo alteration as well as the enamel in part, the latter being popularly known as "burnt" (*verbrannt*).

6. Riddle quotes the following molecular formula for an excellent American powder enamel:—

$$\left.\begin{array}{ll} Pb + BaO & 0{\cdot}40 \\ K_2O & 0{\cdot}15 \\ CaO & 0{\cdot}15 \\ ZnO & 0{\cdot}05 \\ Na_2O & 0{\cdot}25 \end{array}\right\} Al_2O_3 \qquad 0{\cdot}15 \left\{\begin{array}{ll} SiO_2 & 1{\cdot}0 \\ B_2O_3 & 0{\cdot}2 \\ SnO_2 & 0{\cdot}2 \end{array}\right.$$

[1] *Transactions of the American Ceramic Society*, vol. ix. pp. 646-660.

This recipe corresponds to the following composition:—

PbO	23·44 per cent.
BaO[1]	9·66 „
K_2O	5·93 „
CaO	2·35 „
ZnO	1·70 „
Na_2O	6·52 „
Al_2O_3	6·44 „
SiO_2	25·46 „
B_2O_3	5·88 „
SnO_2	12·62 „
	100·00 per cent.

In practice this enamel would be produced by mixing together the following raw materials:—

Borax	14·22 kg.
Lead oxide	20·72 „
Zinc oxide	1·49 „
Felspar	30·48 „
Tin oxide	11·15 „
Soda	4·47 „
Sodium saltpetre	2·96 „
Barium carbonate	11·15 „
Limestone	3·36 „
	100·00 kg.

Loss on smelting = 17 per cent.

In this recipe the high barium-oxide content excites attention. Enamel manufacturers are continually endeavouring to avoid barium compounds altogether, and to reduce the content of alkaline earths to a minimum, since both these classes of compound render the enamel brittle and liable to chip. According to Riddle's investigations, the alkali content in the molecular formula may vary between 0·2 and 0·6, fluorides from 0·135 downwards, barium up to 0·45; boric acid ranges from 0·05 to 0·30, and lead oxide from 0·1 to 0·4 (an excess of lead oxide brings about a yellow coloration of the enamel). The alumina content should vary between 0·1 and 0·25, and the silica from 0·75 to 1·25. It is well known that the higher the silica content the more stable is the enamel against

[1] It is understood, as quoted by Riddle, that 0·25 PbO and 0·15 BaO are contained in the molecular formula.

attack by water, etc.; the enamel, however, is more difficultly fusible, less lustrous, and brittle beyond a certain limit.

In this recipe the ratio $B_2O_3 : SiO_2 : \Sigma$ alkali + lead oxide = 1 : 4·3 : 6.

I personally, for reasons already stated, prefer the following powder enamels, which are entirely free from lead, and with which I have been very successful, since they may be adapted in individual cases to the local conditions by a partial alteration of the borax, alkali, or silica content respectively.

7. The following white powder enamel was prepared by mixing—

Borax	200 kg.
Felspar	120 „
Tin oxide	68 „
Clay	20 „
Soda	8 „
Saltpetre	2 „
Cryolite	40 „
Ammonium carbonate	3 „
Fluorspar	2 „
Magnesium carbonate	2 „
	465 kg.

The analysis of this enamel gives:—

B_2O_3	20·33 per cent.
SiO_2	24·46 „
Na_2O	15·42 „
SnO_2	18·86 „
F_2	4·08 „
Al_2O_3	10·39 „
K_2O	5·66 „
MgO	0·28 „
CaO	0·52 „
	100·00 per cent.

Loss on smelting = 25 per cent.

Or expressed as a molecular formula:—

$$\left.\begin{matrix} Na_2O & 0{\cdot}749 \\ K_2O & 0{\cdot}187 \\ CaO & 0{\cdot}032 \\ MgO & 0{\cdot}022 \end{matrix}\right\} Al_2O_3 \quad 0{\cdot}312 \left\{\begin{matrix} B_2O_3 & 0{\cdot}905 \\ SiO_2 & 1{\cdot}279 \\ F_2 & 0{\cdot}655 \\ SnO_2 & 0{\cdot}390 \end{matrix}\right.$$

$SiO_2 : B_2O_3 :$ Alkali : : 1 : 1·2 : 1.

(*b*) *Normal white enamels for moist covering, when the cast-iron object has been previously enamelled with a ground-mass.* This process is most frequently employed in actual practice, since on the one hand absolutely lead-free enamels may be used, while on the other hand the manufacture is simple, more certain when carefully carried out, and furnishes wares possessing the highest durability. Although at the present time a white enamel is only seldom employed in the moist process, yet I propose to make a most instructive comparison of some examples of the above with lead-free enamels, whereby conclusions may be drawn as to the nature of the various fluxes (borax, alkali) employed as substitutes for lead oxide.

8. A customary recipe runs as follows:—

Quartz	37·5 kg.
Borax	24·0 „
Tin oxide	25·0 „
Lead white	15·0 „
Soda	11·0 „
Sodium saltpetre	10·0 „
Ammonium carbonate	7·0 „
Magnesium carbonate	5·0 „
	134·5 kg.

Loss on smelting = 24·6 per cent.

The additions to the fused enamel during the moist grinding are:—

White enamel clay	7 per cent.
Tin oxide	6 „

The analysis of this fused enamel, including the grinding addition, gives:—

PbO	11·15 per cent.
SiO_2	35·54 „
B_2O_3	7·84 „
Na_2O	12·55 „
SnO_2	27·60 „
Al_2O_3	1·93 „
K_2O	1·10 „
MgO	2·27 „
CaO	0·02 „
	100·00 per cent.

And the corresponding molecular formula is:—

Na_2O	0·67			B_2O_3	0·36
PbO	0·16	Al_2O_3	0·07	SiO_2	2·01
MgO	0·16			SnO_2	0·59

The ratio between $B_2O_3 : SiO_2 : \Sigma$ alkali + PbO = 1 : 4·6 : 3.

Before entering into the discussion of the lead-containing cover enamels, I will deal with the composition of another specimen of this class:—

9.	Lead oxide	2·000 kg.
	Quartz	2·500 „
	Borax	0·750 „
	Soda	0·500 „
	Saltpetre	0·250 „
	Boric acid	0·500 „
	Cryolite	0·400 „
		6·900 kg.

The molecular formula reads accordingly:—

PbO	0·447			B_2O_3	0·516
Na_2O	0·552	Al_2O_3	0·076	SiO_2	2·146
				F_2	0·516
				SnO_2	0·165

The loss on smelting = 10 per cent.

Grinding additions:—

Tin oxide	8 per cent.
Clay	3 „

The analysis gives:—

PbO	29·08 per cent.
SiO_2	37·70 „
B_2O_3	10·54 „
Na_2O	9·93 „
SnO_2	7·26 „
F_2	2·90 „
Al_2O_3	2·55 „

The ratio $B_2O_3 : SiO_2 : \Sigma$ alkali + PbO = 1 : 3·6 : 3·7.

From the ratio $B_2O_3 : SiO_2$ we are able to conclude that enamel No. 8 will be harder, *i.e.* more difficult to fuse, than No. 9.

Finally, in order to be in a position to draw every conclusion arising out of our discussion, let us place side by side two further

examples of lead-free enamels which have been found trustworthy in practice for moist covering:—

10.	Borax	50 kg.
	Quartz	50 „
	Felspar	75 „
	Cryolite	20 „
	Soda	10 „
	Saltpetre	6 „
		211 kg.

The smelting loss amounts to 17 per cent.

At the mill were added:—

Tin oxide	12 per cent.
Clay	7 „

of the weight of the fused enamel before the additions were made.

Borax	60 kg.
Felspar	60 „
Soda	4 „
Cryolite	20 „
Saltpetre	3 „
Clay	2·5 „
Tin oxide	5 „
Magnesium carbonate	0·2 „
Fluorspar	1 „
	155·7 kg.

The smelting loss amounts to 11·3 per cent.

Grinding additions:—

Tin oxide	9 per cent.
Clay	7 „

The analysis of No. 10 gives:—

SiO_2	49·62 per cent.
B_2O_3	8·60 „
Na_2O	11·78 „
SnO_2	9·93 „
F_2	3·42 „
Al_2O_3	10·47 „
K_2O	6·11 „
MgO	0·04 „
CaO	0·03 „
	100·00 per cent.

Molecular formula :—

$$\left.\begin{array}{ll} Na_2O & 0{\cdot}741 \\ K_2O & 0{\cdot}253 \\ CaO & 0{\cdot}002 \\ MgO & 0{\cdot}004 \end{array}\right\} Al_2O_3 \quad 0{\cdot}397 \left\{\begin{array}{ll} B_2O_3 & 0{\cdot}479 \\ SiO_2 & 3{\cdot}200 \\ F_2 & 0{\cdot}702 \\ SnO_2 & 0{\cdot}273 \end{array}\right.$$

$$B_2O_3 : SiO_2 : \Sigma \text{ alkali} = 1 : 5{\cdot}7 : 2.$$

The analysis of No. 11 gives :—

SiO	30·65 per cent.
B_2O_3	15·11 „
Na_2O	15·12 „
SnO_2	11·20 „
F_2	6·88 „
Al_2O_3	13·10 „
K_2O	7·16 „
MgO	0·12 „
CaO	0·66 „
	100·00 per cent.

Molecular formula :—

$$\left.\begin{array}{ll} Na_2O & 0{\cdot}720 \\ K_2O & 0{\cdot}218 \\ CaO & 0{\cdot}033 \\ MgO & 0{\cdot}009 \end{array}\right\} Al_2O_3 \quad 0{\cdot}39 \left\{\begin{array}{ll} B_2O_3 & 0{\cdot}63 \\ SiO_2 & 1{\cdot}53 \\ F_2 & 1{\cdot}05 \\ SnO_2 & 0{\cdot}222 \end{array}\right.$$

$$B_2O_3 : SiO_2 : \Sigma \text{ Alkali} = 1 : 2 : 1{\cdot}5.$$

No. 10, so prepared, is a cheap enamel moderately difficult to fuse ($B_2O_3 : SiO_2 = 1 : 5{\cdot}7$), while No. 11, on the contrary, is an enamel fused at a lower temperature in the muffle-furnace upon the grounded cast iron. The greater silica content in No. 10 is partly compensated for by the higher alkali percentage.

The average for the ratio of $B_2O_3 : SiO_2 : \Sigma$ alkali + lead oxide in the white cover-enamels mentioned is 1 : 3·4 : 2·3, while the average ratio for the same components in the ground-mass amounts to 1 : 9·1 : 1·2. For ground-masses, the ratio of the silica content to that of the boric acid is accordingly almost three times as great as for white cover-enamels, and the alkali content about double.

The average composition of the *lead-containing* cover-enamel will therefore be :—

PbO	20·00 per cent.
SiO_2	37·28 „
B_2O_3	9·19 „
Na_2O	11·14 „
SnO_2	17·42 „
F_2	1·45 „
Al_2O_3	2·24 „
K_2O	0·65 „
MgO	1·23 „
	100·00 per cent.

The average composition of the *lead-free* cover-enamel will therefore be:—

PbO	—
SiO_2	35·00 per cent.
B_2O_3	14·66 „
Na_2O	14·19 „
SnO_2	13·35 „
F_2	4·86 „
Al_2O_3	11·35 „
K_2O	6·35 „
MgO	0·24 „
	100·00 per cent.

The potash content will naturally be greater or less, according as we have to do with a potash felspar glaze or one with quartz alone. The potash as a rule only enters into the enamel as potash felspar, since in practice sodium carbonate or nitrate is preferred. Further, we have the fact that in one case 20 per cent. lead oxide is replaced by the equivalent amount of boric acid. Twenty per cent. lead oxide corresponds to an equivalent amount of 5·5 per cent. boric acid ($PbO : B_2O_3 = 223 : 62$).

It is indisputable that enamels containing lead possess very attractive qualities with regard to brilliant appearance, lustre, ready fusibility, and cheapness. On the other hand, it has been firmly established that in the case of enamel glazes the lead oxide may be completely replaced by borax or boric acid plus alkali.

The molecular formulæ corresponding to the two types of enamel cited above are accordingly:—

PbO	0·322	Al_2O_3	0·067	B_2O_3	0·419
Na_2O	0·579			SiO_2	2·000
MgO	0·096			F_2	0·225
				SnO_2	0·354
Na_2O	0·747	Al_2O_3	0·374	B_2O_3	0·68
K_2O	0·220			SiO_2	2·00
CaO	0·033			F_2	0·85
MnO	0·002			SnO_2	0·34

In general, when dealing with the influence of the most important raw materials on the enamel, it may be stated that the more readily fusible the enamel in consequence of its boric acid or alkali content, the greater the loss on melting.[1] Boric acid is a most excellent flux, producing a brilliant surface effect, but is fairly expensive and easily fusible. Enamels with an excessive content of boric acid are not very permanent under the influence of water and of the atmosphere. A somewhat harder enamel will therefore in general be preferred, and consequently must contain less borax and alkali, notwithstanding a certain deficiency in lustre.

In enamels containing lead, the content of lead oxide should not exceed 25 per cent. For superior white enamels I can recommend the employment of ammonium carbonate, in spite of the contradiction which appears to be involved therein that this salt volatilises at the heat of the furnace. Experience in important works, however, proves that the addition of ammonium carbonate prevents the so-called *chipping* or *parting* of the enamel. An explanation of this phenomenon is still wanting. Appreciable amounts of barium and calcium compounds must be entirely avoided. The employment of large quantities of fluorspar, therefore, can scarcely be recommended for the manufacture of our enamels, notwithstanding the cheapness of this flux.

The preparation of the ground-mass and cover enamel for cast-iron utensils requires extraordinary care and experience. Hand in hand with the latter must go a suitable composition of this cast iron.[2] As a rule it should contain 3·5 per cent. carbon, 2 per cent. silicon, 1·4 to 1·8 per cent. phosphorus, and 0·5 to 0·7 per cent. manganese.

[1] The *smelting loss* of an enamel is the loss which the mixed raw materials undergo when melted in the furnace. This loss can vary for ground-masses between 10 and 15 per cent., and for cover enamels between 14 and 28 per cent.

[2] See J. Grünwald in *Stahl und Eisen*, 27th January 1909, p. 137.

Further, an appropriate firing of the enamelled wares must be carried out in the muffle-furnace, whereby oxidising gases proceeding from the combustion or from impurities in the coal must be avoided, otherwise the enamel will become dull and dirty (in consequence of the partial reduction of the metallic oxides, especially in the presence of lead oxide). As a rule, for opaque-producing materials only the best tin oxide and cryolite are employed by first-class and reliable firms; for some years the endeavour to replace these materials by cheaper substitutes has only met with moderate success.

CHAPTER VII.

THE STIFFENING OF ENAMELS WHEN GROUND MOIST BY MEANS OF VEHICLES.

The enamel, which has been fused in the furnace, is finely ground in the wet mill (stone or drum mills) with about 30 to 38 parts water and 4 to 8 parts enamelling clay, and passes to the enamel works in this condition. The enamel is then said to be ready for covering (Auftragfertig).

If the clay addition were omitted, the ground enamel would quickly settle to the bottom and not only be troublesome to remove from the mill, but make manipulation with it practically an impossibility. The clay addition has, indeed, not only the property of rendering the enamel mass cheaper, of exerting an opaque-producing influence, and, within certain limits, of being an excellent regulator of the fusion, but also of enveloping the fine enamel particles levigated in the water and holding them in suspension. The clay, therefore, confers upon the enamel that uniform consistency which is absolutely necessary for proper manipulation. Very frequently, however, a clay addition alone is insufficient to impart the necessary tenacity to the ground enamel. The practical man requires the moist ground enamel to stand and not run, *i.e.* a sample allowed to flow out slowly from the ladle must cease to move after some seconds, or at the most it should not pass out in disconnected drops or lumps. The process of bringing an enamel to a definite consistency or tenacity, by the addition of small quantities of dissolved or also of undissolved salts, is termed the *setting* (Einstellen) of the enamel. The chemical compounds employed for this purpose are known as *vehicles* or *stiffening materials.*

The literature dealing with this question is still very meagre. In a work by Bock [1] the vehicles are reviewed without, however,

[1] *Chem. Ztg.*, 1909, No. 13, p. 109.

any theoretical explanation of their mode of operation being put forward. In the light of a correct theory the somewhat divided opinions of experts might receive correct judgment. The practice in large works, which has been found most advantageous, is to add the vehicle not at the mill, but just before performing the enamelling process and therefore in the working dishes.

The delicate operation of setting should naturally be carried out by an expert or only by quite trustworthy and skilled workers: too great an addition of vehicle is even as inadvisable as the attempt to render a too dilute enamel consistent by pressure, instead of the better method of allowing the excess water present to be removed by settling or by the immersion of clean hot firebricks. The vehicle must only be used in cases where absolutely essential, and, in addition, excess water should be carefully avoided when grinding the enamel, since such an enamel will set with difficulty, run strongly, and require the addition of unnecessarily large amounts of vehicle. Further, it may be emphasised that after the vehicle addition the enamel must be well stirred and allowed to stand five to ten minutes before beginning to work with it. The action of the vehicle is similar to a reaction requiring a definite time for completion. Moreover, to the practical man it is a well-known fact that the activity of the vehicle abates after some hours, from which it follows that it is inadvisable to set too large quantities of enamel at a time.

Which are the possible vehicles? They are those acids, alkalies, and salts, in short, those compounds which from the standpoint of modern physical chemistry are termed electrolytes. The dissociation theory informs us that acids, alkalies, and salts are split up more or less when in solution into ions which are electrically charged, viz. into the positive kations ($H^{\cdot}$, $K^{\cdot}$, $Na^{\cdot}$, $Mg^{\cdot\cdot}$, etc.) and into the negatively charged anions (the acidic radicals SO_4'', Cl', OH', etc.). Only modern physical chemistry is in a position to explain certain phenomena connected with the setting of enamels, especially such facts as the capability of an enamel to be set or stiffened by the addition of acids such as HCl, bases like ammonia, caustic soda and soda, or salts such as $MgCl_2$, $MgSO_4$, $Na_2B_4O_7$, etc.

The following vehicles are found in use: Hydrochloric acid (HCl), common salt (NaCl), Epsom salts ($MgSO_4$), Glauber's salt (Na_2SO_4), borax ($Na_2B_4O_7 \cdot 10H_2O$), calcined magnesia (MgO), anhydrous soda (Na_2CO_3), sal-ammoniac (NH_4Cl), and ammonium

carbonate ($(NH_4)_2CO_3$), or more correctly ammonium sesqui-carbonate, which is a mixture of ammonium bicarbonate with ammonium carbamate ($(NH_4)HCO_3 + NH_2CO_2NH_4$). For ground enamels, a solution of cobaltous chloride ($CoCl_2$) has been described as an excellent vehicle. Clay also has a setting influence upon enamel, but this is generally insufficient. A selection must now be made from the large number of vehicles comprising those in actual use and possible ones most worthy of recommendation :—

Ammonium carbonate is suitable for all enamels, being perfectly harmless, and decomposing at the fusion temperature of the enamels into its volatile components, carbon dioxide and ammonia. *Sal-ammoniac* is also readily volatile, but I give the preference to ammonium carbonate, since within the furnace the free hydrochloric acid generated from the sal-ammoniac may possibly form compounds with the separate bases of the enamel ; chlorides are known to have an injurious effect on the appearance of the fired wares, as they, as also sulphates, readily produce flaws in the enamel surface during storage in the warehouse.

Magnesium oxide (MgO) deserves the highest recommendation as a vehicle for white enamels, while magnesium carbonate ($MgCO_3$) is to be avoided. As a precaution, the magnesium carbonate may be placed in a clay vessel and heated to redness for several hours in the muffle-furnace until by loss of carbonic acid the whole has been changed into burnt magnesia (magnesia usta, MgO). For this operation a sufficiently high temperature is required together with a certain interval of time, since the conversion of carbonate into oxide only takes place slowly. In practice a trustworthy sign that the magnesium carbonate after being heated to redness has completely changed into oxide is given by dipping a finger into the cooled, previously ignited magnesium oxide, and slowly drawing it out; if none or only a little white powder adheres to the finger, the magnesium carbonate has been sufficiently heated. Another test is to add dilute acids to the levigated magnesia, whereby from the gas evolution an opinion may be formed as to the presence of undecomposed magnesium carbonate.

A third vehicle worthy of recommendation, especially for ground enamels, is *borax* ($Na_2B_4O_7$) which has been previously fused and pulverised and is soluble in hot water.

The burnt magnesia is finely stirred with a little water and enamel, forced through a wire sieve No. 40, and intimately mixed

in the working dishes with the white enamel. The three harmless vehicles already mentioned completely suffice. The real action during the setting of an enamel is bound up with the presence of clay as a grinding addition. An enamel ground without clay is scarcely capable of being stiffened. The setting of enamels, brought about by the influence of vehicles, must accordingly be traced to an action between clay and electrolyte. Whitney and Alonzo Straw [1] had previously shown that suspensions of clay in water may have their stability strengthened by small additions of alkali; on increasing the alkaline addition, however, they become more thinly liquid again. On the question of the liquefaction of clay by addition of alkalies, we have to thank Böttcher's extremely valuable results.[2] By the small addition of alkalies to suspended clay, liquefaction first ensues, followed, however, by stiffening when greater amounts are added. Böttcher found that according to the concentration of the alkalies added, the stiffening of the clay takes place more slowly or more rapidly again into the thinly liquid condition. Also during the setting of the enamel, it has been noticed that the setting activity, *i.e.* the stiffness of the enamel, decreases after some time. Thereby it was demonstrated, for example, that caustic soda is an inferior stiffening agent to caustic potash.

The clay particles suspended in water are to be regarded as a negatively charged colloidal solution, and may be precipitated as a hydrogel by oppositely charged electrolytes. The clay colloids are present in the gel form: in order to prevent these from passing over into colloidal solution, *i.e.* into hydrosol, very small amounts of salts suffice, *e.g.* $Ca^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ ions, since the coagulating power of the divalent ions towards certain sols is about sixty times, and that of the trivalent ions about 600 times, greater than that of the monovalent.[3] The deflocculation of a clay containing a soluble calcium salt, *e.g.* gypsum, which is brought about by soda, takes place according to the following formula:—

$$\text{Ca with gel} + Na_2CO_3 \Rightarrow CaCO_3 \text{ insoluble} + Na_2 \text{ with sol.}$$

By further addition of soda the number of Na ions is increased, and according to Förster flocculation generally appears. The action of ammonia (as vehicle) upon clay has been explained as

[1] *Journal of the American Chemical Society*, vol. xxix. p. 325.
[2] *Sprechsaal*, 1909, No. 14, p. 200, etc.
[3] *Sprechsaal*, 1910, No. 9, p. 119.

dissolving the vegetable clay acids and by insufficient water addition forming gelatinous ammonium humate. The action of sal-ammoniac and ammonium carbonate may be similar. After the addition of vehicle to the enamel, stiffening ensues, which, according to the evidence, may be traced to the precipitating action of water containing silicic acid, to which indeed the great precipitating ability of small quantities of vehicles may be due. Whether, when setting an enamel by vehicle addition (electrolytes), we have to do with a transformation of the colloidal hydrosols present in every clay, a position we are readily inclined to adopt, must first be made clear by thorough investigation. In this respect the addition of water-glass solution (Na_2SiO_3) to the enamel is interesting. By small additions, a dilution of the moist ground enamel takes place, while with increasing amounts the whole mass stiffens and gradually becomes solid.

Soda is still often used as a vehicle. Notwithstanding its excellent setting capacity, however, its use should be avoided as far as possible, since it often occasions the dulling and efflorescence of the enamel (transition from the amorphous to the crystalline condition).

Ammonia solution would be a very good vehicle but for the annoyance caused by its disagreeable odour, and the fact that its action as an enamel-stiffening medium is not sufficiently prolonged.

A decisive warning must be uttered before using acids as stiffening agents for blue enamels, owing to facts which were observed by me in a large works under rather curious circumstances.

Let us collect our results in a few concise sentences as follows. The stiffening power of a vehicle is bound up with the presence of clay in a moist ground enamel. Vehicles are electrolytes in the light of modern physical chemistry, *i.e.* acids, alkalies, or salts of an inorganic character. Those electrolytes should be employed as vehicles which decompose entirely, or in part, at a temperature below the melting- or softening-point of the enamel into volatile components such as ammonia, carbonic acid, hydrochloric acid, sulphuric acid, etc., or which, in general, consist only of an alkaline earth oxide such as magnesia, or of a borate such as borax. Ammonium carbonate, well-calcined magnesia, and fused borax soluble in hot water, are the most harmless, the safest, and the vehicles most worthy of recommendation. Unburnt clay itself

possesses the ability to stiffen, but when used alone is generally of insufficient power. Chlorides or sulphates are to be rejected as vehicles. In general one endeavours to manage without vehicles, or at all events with a minimum quantity; this is facilitated by a suitable clay addition, by avoiding unnecessary amounts of water at the mill or in the working dish, and by allowing the enamel in its final moist ground state to stand in tubs from eight to fourteen days.

CHAPTER VIII.

AN ARTICLE DEALING WITH THE HEATING AND PICKLING OF THE ROUGH IRON WARES IN THE ENAMEL INDUSTRY.

THE modern enamelling industry, *i.e.* the technique of covering sheet- or cast-iron wares with an enamel glaze coloured by metallic oxides, has made enormous progress during the last decade. Germany employs therein about 25,000 workers in round numbers, and the annual output is estimated at 60 million marks. Austria-Hungary follows immediately after Germany in importance. France, Belgium, Switzerland, and recently Italy and Spain, possess enamel industries of growing significance. The enamel industry counts to-day among the most important purchasers of sheet iron, and in this regard Dr H. Wuppermann[1] estimates the annual consumption of sheet iron at 70,000 to 85,000 tons, having an average value of 17 to 20 million marks.

Heating.—The processes of heating to redness and pickling have an essential influence upon the production of faultless enamelled objects. The earlier empirical views which prevailed with regard to the influence of the different works' operations upon the success of the finished article were not to the advantage of the industry, and had to give place to the teachings of modern technical chemistry, which sought to investigate the individual processes during manufacture, and so brought about the recent progress enjoyed by our industry. The stamped or pressed rough sheet ware is heated to redness for the removal of the grease and dirt layer (due to previous operations). The importance of the heating process is not exhausted, however, with the combustion of the fat. For acquiring a well-finished article the use of a first-class, box-heated, doubly forged basic Martin steel is indispensable.

[1] H. Wuppermann, *Die Industrie emaillierter Blechgeschirre in Deutschland*, Karlsruhe, 1907.

Inferior kinds of steel, such as are often used for some cheap folded articles, are in reality of no advantage when one considers the greater percentage of imperfect goods produced, and the insignificant difference in price between the doubly forged and singly forged varieties of sheet steel. Consequently the manufacturer uses almost throughout only the very best German brands, which are absolutely equal to the English forged steel preferred earlier. The following is regarded as a favourable composition for a good forged steel:—

Carbon	0·05 to 0·08 per cent.
Phosphorus	less than 0·03 „
Manganese	0·25 to 0·35 „
Silicon in small amounts	0·02 „

The strength test must show the following results:—

Coefficient of tenacity	35 to 38 per cent.[1]	
„ elasticity	30 to 35 „	
„ contraction	60 „	in round numbers
Specific gravity	7·6 to 7·8	

For utensils a cast iron of the following composition is generally used:—

Carbon	3·5 per cent.
Silicon	2·0 „
Phosphorus	1·4 to 1·8 „
Manganese	0·5 to 0·7 „

while for weak-walled objects 1 to 2 per cent. of pure steel fragments are added.

Besides the chemical process, which includes the combustion of the organic substances as well as the surface oxidation of the iron, an important physical effect must still be emphasised, viz. of imparting to the iron wares the favourable malleability and softness which the forged steel originally possessed, but which it had partly lost during the course of the mechanical operations of drawing, stamping, planing, and pressing. By heating the rough wares to redness on scientific lines, many flaws which have been frequently assigned to other causes may be avoided.

Next to a correctly chosen enamel, the most important part in

[1] Julius Grünwald, *Theory and Practice of Enamelling on Iron and Steel.* C. Griffin & Co., Ltd., London, 1909.

the production of durable enamelled wares is played by the well-conducted heating of the rough wares. The heating of the rough sheet-iron wares is carried out according to different systems:—

1. In closed, air-tight, iron cylinders, which are exposed to direct flame heating or to indirect heating by means of radiation from red, glowing incandescent chambers.

2. By simply heating to redness in the muffle-furnace.

3. By heating to redness in perpendicular shaft-furnaces, whereby the rough wares are laid in sheet-iron baskets which move uninterruptedly along endless chains and are carried to a certain position of the flames from a gas generator plant.

4. The rough wares set in cylinders are placed in fireproof trucks. These small trucks move automatically in a horizontal walled channel in the middle of which play the flames from generator gases, whereby the wares during their passage are heated to a red heat.

A whole series of heating systems are in existence, and the choice must be made according to the following principles:—

1. The heating will exert a more advantageous influence upon the rough ware to be enamelled, the more efficacious the air-tightness during the heating and the more slowly this takes place, also according as the cooling of the hot ware is accomplished very gradually and by avoiding access of air as far as possible.

2. It is important that sufficient space be allowed between the individual articles to be heated. A too thorough packing together of the pots, washing utensils, etc., during the heating operation, must therefore be avoided as far as practicable.

3. The flame control must be of such a kind that the heating cylinder is uniformly surrounded, and a uniform heating thereby brought about by avoiding a thin flame.

4. The duration of the heating must not exceed a definite interval depending on the nature of the crude ware. The temperature on an average should range from 750° to 850° C. The construction of the furnace should be entrusted to specialised firms.

The choice of one or other of the heating systems must be based upon the compass of the production, the quality of the wares to be prepared, and the proportion of space at disposal. A rough ware heated correctly with absence of air, exhibits a uniformly black, often velvet-brown colour. The heating of cast-iron utensils

for enamelling purposes is generally carried out in the muffle-furnace.

Pickling.—After the rough ware has been heated to redness, it is then pickled. The object of pickling is to dissolve away the black surface layer of iron oxide (Fe_3O_4). The ware thereby acquires a clean metallic surface, which for the further operations is absolutely necessary. As a rule the process is carried out with hydrochloric acid, more seldom in a sulphuric acid bath. The mixture employed is made up of 1 part hydrochloric acid of 21° Bé. (sp. gr. 1·171), with 2 parts water, or 15 parts concentrated sulphuric acid of 65° Bé. (sp. gr. 1·79 to 1·8) with 85 parts water.

In both cases the use of acids free from arsenic is recommended, since the arsine thereby developed has an injurious effect upon the workmen engaged in pickling. The *test for arsenic* in the hydrochloric or sulphuric acid is advantageously made according to the published method of E. Seybel and H. Wikander, improved by N. G. Blattner and J. Brasseur.[1] The method depends upon the reaction between potassium iodide and the arsenic contained in the acid.

$$As_2O_3 + 6HCl + 6KI = 2AsI_3 + 6KCl + 3H_2O.$$
$$As_2O_5 + 10HCl + 10KI = 2AsI_5 + 10KCl + 5H_2O.$$
$$AsI_5 = AsI_3 + I_2$$

Blattner and Brasseur add a standard potassium iodide solution to the hydrochloric acid to be tested, filter through glass wool, dissolve the residue of arsenic tri-iodide in water, saturate with pure sodium carbonate, add a little starch paste solution, and titrate with $\frac{N}{10}$ iodine solution until the blue colour remains.

$$\frac{\text{The number of c.c. } \frac{N}{10} \text{ iodine solution} \times 2 \times 0{\cdot}00375}{\text{Specific gravity of the acid}} = \text{the percentage of arsenic in the acid tested.}$$

The quantitative test for the arsenic in sulphuric acid is made in a similar manner.

$$\frac{\text{The number of c.c. } \frac{N}{10} \text{ iodine solution used} \times 4 \times 0{\cdot}00375}{\text{Specific gravity of the sulphuric acid}} = \text{percentage of arsenic.}$$

The rough ware remains from thirty to forty-five minutes in the

[1] *Chemiker Ztg.*, 1902, No. 5, p. 50, and 1904, p. 211.

acid bath, which is warmed by means of steam from 20° to 30° C. (when pickling with sulphuric acid the temperature is as a rule from 70 to 80° C.), then the article is washed with water, scrubbed, washed and placed in boiling soda solution so as to neutralise any residual acid. From the soda bath it is taken to a hot drying hearth. Acid baths freshly compounded are inactive at the beginning, and therefore some old pickling liquid, which has stood for some time, is added with advantage. This phenomenon may be explained as due to catalytic agents, called into being during the gradual formation of hydrogen. Too concentrated acid acts more slowly, but is more destructive. By the pickling process one acquires not only a clean metallic surface capable of taking enamel, but also a certain roughness which is advantageous for the enamelling process to follow. The enamel will remain firmer and more intimately adherable to the metallic surface, or, in other words, will unite more permanently with it by filling up the small surface cavities. We see, therefore, that excessively smooth metallic surfaces are less fitted for enamelling purposes.

The heating and pickling of the rough wares causes a not unimportant loss of metal, which may be estimated as averaging 4 per cent. Accepting the total annual consumption for the German sheet-enamelling industry at 75,000 to 80,000 tons, the heating and pickling loss therefore attains the respectable amount of 3000 to 3200 tons yearly. It would be much beyond the scope of this work were we to go more intimately at this stage into the utilisation of these pickling residues and dissolved iron salts, or into the legally prescribed process for the purification of the pickling effluent. For cast-iron utensils the average heating and pickling loss is estimated at about 0·3 per cent.

For the more profitable use of the pickling agents various proposals have been made, of which the following deserves mention. The process depends upon a regeneration of the hydrochloric acid from the ferrous chloride by the addition of small amounts of sulphuric acid :—

(i.) $2HCl + Fe + xH_2O = FeCl_2 + H_2 + xH_2O$.
(ii.) $FeCl_2 + H_2SO_4 + xH_2O = FeSO_4 + 4H_2O + 2HCl$.

The dibasicity of sulphuric acid must be taken into account when making the addition.

By the skilful determinations of daily analyses a material economy may be effected. For cast-iron pickling an 8 to 10 degrees

sulphuric acid solution may be recommended, or according to Sorel,[1] a mixture of 96 parts sulphuric acid of 10° Bé. and 4 parts tin salt ($SnCl_2$) or zinc chloride ($ZnCl_2$). Recently baths have been used in which the pickling solution is maintained in continual motion, whereby a mechanical action, and therefore an accelerated solution, of the oxide layer, is brought about. By bubbling air through, or by the addition of old sheet zinc parings, the pickling liquid will also be set in motion.

The study of pickling processes deserves our best attention, since, according to recent investigations, they exert great influence upon the quality of the sheet steel. It is well known that steel wire deteriorates in quality after pickling, if its original physical properties are not restored by subsequent heating at about 130° C. In the separate phases of the process, viz. (1) before pickling, (2) after pickling, (3) after drying, (4) after again firing, the following has been found with regard to the change in resistance of the steel:— The strength test carried out upon a Riehl machine gave for 1 to 3 the same maximum resistance. The bending test, on the contrary, showed a decline in the resistance to bending of the pickled ware, and a return of the previously pickled ware, when heated at 130° C., to its original condition.

An enrichment of hydrogen molecules in the pickled iron objects, due probably to catalytic processes, may reasonably be accepted. Ledebur has already pointed out that the change produced in the physical properties of iron during the pickling process decreases according as the content of certain foreign substances increases. A silicon content in particular reduces the injurious action of the pickle, while a carbon content exerts a contrary influence. It therefore follows from the above that steel is more sensitive towards pickling than soft wrought iron, while grey pig iron with 1 to 2 per cent. silicon is scarcely altered, even after lying for several days in weak pickling acids. The more compact the texture of the iron object to be pickled, the greater its resistance to attack and corrosion. Therefore sheet-steel utensils having a surface too smooth (produced by planing and pressing, etc.), and in consequence too compact, will be less readily attacked by the pickling, a fact which, in our particular case, is disadvantageous for enamelling purposes.

Just as rusted objects on long standing lose their tendency to crack, so the same effect can be produced on pickled wares by

[1] *Dingler's Polyt. Journal*, cvii. 446.

subsequent heating in a boiling soda bath, and then rapidly drying the wares upon special hearths such as are used in the pickling department of an enamel works. We see, therefore, that it is absolutely necessary to restore the original physical properties to the heated and pickled rough wares by allowing them to stay in boiling soda solution (whereby also the last traces of acid are neutralised), and then rapidly drying them upon heated drying hearths. Electrolytically prepared iron, *i.e.* chemically pure iron, is attacked by the pickle forty times more strongly than iron which has been also produced electrolytically, but heated to redness before pickling.

Corresponding to the youth of modern enamelling technology, we are still uninformed with regard to all the chemical and physical changes which take place during the course of manufacture. Much further work will still be required in order that the extremely interesting subject of enamelling, which is to-day of such great economic importance, may have its depths plumbed and its secrets disclosed. The meagre amount of work hitherto published should serve as a foundation for the building up of the chemistry of the enamel industry.

CHAPTER IX.

RECENT INVESTIGATIONS ON THE PICKLING PROCESS.

The operations of heating to redness and pickling count among the most important of the preparative processes in the industrial working-up of iron and steel. On this subject I have already made a short communication in another place.[1] Recently, different publications have appeared dealing with the influence of the heating and cooling processes, and also with the nitrogen and hydrogen content in the iron, while proposals have been submitted for the scientific pickling of iron objects. Before I discuss the recent theories respecting steel pickling, I will briefly collect together the most important results of later research upon the effect of heating iron to redness and the content of occluded gases. The best heating temperature varies between 670 and 720 C., and will be lower the less the carbon and manganese content of the iron.

According to Wawrzinirk,[2] the elasticity limit lies below the malleability limit. The maximum flexure-strength is found, as a rule, with a carbon content of 0·9 per cent. The extension coefficient decreases with increasing carbon content, similarly to the modulus of elasticity. By allowing iron which has been heated to redness to cool slowly, the formation of ferrite is increased. According to Hjalmar Braune,[3] the occluded gases in a sample of Martin steel amount to 30·8 per cent. by volume of nitrogen and 67 per cent. by volume of hydrogen, or an average 0·085 per cent. nitrogen. By dissolving the iron in hydrochloric acid, the greatest part of the occluded nitrogen is transformed into ammonia. A small part of the nitrogen in this solution process is transformed into carbamine. According to the publications of A. S. de Osa,[4] iron can occlude 27 times its volume of hydrogen, and cement steel

[1] *Stahl und Eisen*, 1909, p. 137.
[2] *Metallurgie*, 1907, pp. 810–815.
[3] H. Helgesen, *Bulletin de la Société de l'Industrie Minerale*, 1907, vol. vii. p. 494.
[4] *La Métallurgie et la Construction Mécanique*, 15th April 1908.

as much as 120 times. All these investigations are contributions towards the explanation of the varied and hitherto mysterious occurrences on heating and pickling iron objects.

In many industries such as those of enamelling, tinning, galvanising, and electrotyping, an absolutely clean metallic surface, free from grease and rust, is necessary for the steel objects. For this purpose the rough ware is heated to redness in a special furnace (*e.g.*, muffle and similar ones), whereby on cooling in the air the formation of a layer of black oxide of iron takes place. This layer may be removed (1) by the mechanical attack of a sand blast[1]; (2) by acid pickling; (3) by electrolytic means.

Sand Blast.—For smaller articles the sand blast is too dear, on account of the high working expenses and restricted output. On the other hand, it is employed with advantage for large pieces, and especially for cleaning cast-iron wares previous to enamelling.

Acid Pickling.—At present the pickling process is usually carried out in an acid bath, using either dilute hydrochloric or sulphuric acids, while for cast-iron objects dilute hydrofluoric acid finds frequent application. The activity of the pickle is a function of the concentration and purity of the acid; the latter condition is unfortunately often ignored.

The temperature of the bath is also of essential importance, as well as the quality of the iron and the purpose for which the pickling is intended. Burgess[2] found that 1 kg. commercial hydrochloric acid in proportion to 1 kg. sulphuric acid possesses a solution-ability of 10 : 19. The choice of acid, however, depends also on its price; in the neighbourhood of certain chemical works hydrochloric acid is delivered cheaper than sulphuric, but by transport the price of the former rises disproportionately. For pickling, previous to tinning and zincing, hydrochloric acid has absolute preference.

Sulphuric acid, especially in warm pickle baths, is troublesome to manipulate, producing irritating coughs, and requiring extensive ventilation; moreover, the pickled sheet-iron object is frequently observed to acquire a blackish colour, due to the formation of a thin coat of iron sulphide. R. Kneitsch found[3] that cast iron was badly suited for storing fuming sulphuric acid or as a pickle vat, since not only was the cast iron attacked, but also explosions could

[1] Compare *Stahl und Eisen*, 1909, p. 392 *et seq.*

[2] *Electrochemical and Metallurgical Industry*, 1905, vol. iii. pp. 384–386.

[3] Compare R. Kneitsch, "Sulphuric Acid and its Preparation," *The Mineral Industry*, vol. x. pp. 605–635.

frequently take place. He explains these phenomena by assuming that the fuming sulphuric acid penetrating into the pores of the cast iron is reduced in part to gaseous sulphur dioxide and also to sulphur trioxide, while a part of the carbon in the cast iron is transformed into carbon dioxide. How far his explanation of the above facts is correct, remains to be tested by further investigation. He assumes that the gases formed at a low temperature produce pressures in the interior of the cast iron. On the other hand, it is a well-known fact that dilute sulphuric acid may be stored without danger in cast-iron utensils.

Hydrochloric acid may be employed at greater concentration than sulphuric. Hydrochloric acid of 10° Bé. contains 43 per cent. by weight of 22° acid, while sulphuric acid at the same degree Baumé contains only about 11 per cent. by weight of concentrated 66° acid.

Sulphuric acid below 10 per cent. acts slowly in the cold, and only becomes really active when the bath is warmed. In practice the concentration of the sulphuric acid employed is limited by that density which is necessary for maintaining in solution the sulphates formed. The chlorides of iron are more soluble than the sulphates; the latter makes possible the use of hydrochloric acid in a more concentrated condition: 1 part of ferrous chloride requires 6·68 parts of cold water for solution: 1 part of ferric chloride needs 0·63 parts of cold water, and 1 part ferrous sulphate 1·64 parts cold water for solution.

Dealing with the purity of the acids employed, the presence of arsenic plays an important part, since it appreciably diminishes the rate at which the iron is dissolved by pickling, in addition to the injurious effects upon health from inhaling the arsine which is developed. Upon the former of the above facts is based the rust-preventing action of arsenic.[1]

The dissolving away of the black iron-oxide layer from the iron object by pickling, is a mechanical operation. The acid penetrates through the porous oxide layer to the metallic surface, and dissolves a part of the iron with formation of hydrogen, which, being contained between the metallic surface and the oxide layer, removes the latter by pressure, causing its accumulation at the bottom of the pickling vessel as a mud. We shall see later that the recent electrolytic pickling process proposed by C. J. Reed is in exact opposition to this. Although iron oxide is only sparingly

[1] Lindet, *Société Chimique*, 1905.

soluble in acids, yet by allowing the so-called pickle mud to stand at the bottom of the vessel for some time, an unnecessary acid consumption is incurred. Burgess has submitted a method by Cowper-Coles, who proposes to remove periodically the magnetic iron oxide which settles on the floor of the pickle-vat by means of a magnet. A simpler method for accomplishing the same object is to decant the acid baths frequently. For certain brands of manufactured metallic wares this cannot be insisted upon too strongly, in order to prevent the penetration of the mud into the rolled edges of utensils, etc.

I have already in another work dealt with the inactivity of a freshly-compounded pickle bath.[1] Only after several hours, *i.e.* when a sufficient amount of hydrogen has been developed in the bath, or by the addition of some pickle acid seasoned with this gas which has been decanted from a previous operation, does a pickling and solvent action set in. Here in all likelihood are catalytic reactions whose study would be of much interest.

The loss in sheet iron to the enamelling industry during the pickling process varies, for example, with medium sheet iron of 0·3 to 0·5 mm. thickness between 4·1 and 2½ per cent. For cast-iron wares an average loss of 0·3 to 0·4 per cent. is suffered. The

THE LOSS IN SHEET IRON DURING PICKLING.

Diameter of the Sheet-iron Disc in cm.	Thickness of the Sheet Iron in mm.	Surface in sq. cm.	Weight of the rough ware in Grms.		Loss on Pickling (Sheet-iron Loss), per cent.
			Before Heating and Pickling.	After Pickling.	
20	0·25	628	55	52·25	5
,,	0·30	,,	66	63·25	4·18
,,	0·35	,,	77	74·25	3·50
,,	0·40	,,	88	85·25	3·10
,,	0·45	,,	99	96·25	2·80
,,	0·50	,,	110	107·25	2·50
,,	0·55	,,	121	118·25	2·30
,,	0·60	,,	132	129·25	2·10
,,	0·65	,,	143	140·25	1·90
,,	0·70	,,	154	151·25	1·80
,,	0·75	,,	165	162·25	1·70
,,	0·80	,,	176	173·25	1·50
,,	0 85	,,	187	184·25	1·40
,,	0·90	,,	198	195·25	1·38
,,	0·95	,,	209	206·25	1·31
,,	1·00	,,	220	217·25	1·25

[1] *Stahl und Eisen*, 1909, p. 138.

preceding table[1] should be of interest in this connection. Some statements made by Burgess[2] have been corroborated by my experiments. For better interpretation I have set out the results of my investigations in the form of quantitative tables and diagrams. The conclusions are easy to draw therefrom.

Sheet-iron discs of 10 cm. diameter and about 0·75 mm. thickness were chosen for the experiments. All the discs were cut from the same plate of English basic Martin sheet steel. The metal possessed the following chemical composition :—

C = 0·00 per cent., Mn = 0·24 per cent., P = 0·04 per cent.

The pickling test was carried out according to the usual methods employed in iron-ware manufacture, approximating as near as possible to the actual manufacturing processes. In the first series of experiments the temperature of the pickling bath was 60°, and in the second series 18° C. The experiments were carried out with both hydrochloric and sulphuric acids, and their object was to establish the relationship between the duration of heating to redness, temperature of the red heat, velocity of the pickle attack, and temperature of the pickling bath. The experimental discs were heated in the muffle-furnace for exactly three minutes, the temperature being determined by means of Seger cones at 550° C., 670° C., and 940° C.

The following conclusions may be drawn from the numerical Table I. and the diagrams 1, 2, and 3. The experimental discs of 10 cm. diameter have a surface of 157 sq. cm.

The metallic loss after pickling in proportion to the surface of the pickled sheet iron was as follows :—

The loss in metal per 100 sq. cm. surface after pickling amounted to—

gr.				°C.
from 0·4	to 0·5	if heated at		550
„ 0·5	„ 1	„	„	670
„ 3	„ 4	„	„	940

[1] Julius Grunwald, *The Theory and Practice of Enamelling on Iron and Steel*, C. Griffin & Co. Ltd., London, 1909.

[2] *Electrochemical and Metallurgical Industry*, 1905, vol. iii. p. 384 *et seq.* Abstracted and re-arranged by Robert le Chatelier, and printed with incorrect references in the *Revue de Métallurgie*, July 1907, p. 507.

QUANTITATIVE TABLE I.

Number of Experiment . . .	1	2	3	4	5	6	7	8	9	10	11	12
Weight of the sheet disc before heating to redness and pickling, . gr.	31·638	31·960	32·237	32·524	32·214	32·286	31·160	33·773	30·844	32·208	33·760	31·781
The duration of heating in the muffle-furnace in minutes . . .	3	3	3	3	3	3	3	3	3	3	3	3
Temperature of the muffle-furnace in °C.	550	550	550	550	670	670	670	670	940	940	940	940
Weight of the disc after heating in kg.	31·642	31·135	32·251	32·539	32·275	33·391	31·240	33·858	31·809	32·691	34·212	32·117
Increase in weight after heating in gr.	0·004	0·016	0·014	0·015	0·061	0·105	0·080	0·085	0·564	0·483	0·452	0·396
Increase in weight after heating, per cent.	0·012	0·05	0·043	0·046	0·2	0·3	0·23	0·25	1·8	1·5	1·14	1·2
The pickling acid employed . .	HCl	HCl	H_2SO_4	H_2SO_4	HCl	HCl	H_2SO_4	H_2SO_4	HCl	HCl	H_2SO_4	H_2SO_4
Temperature of the pickling bath in °C.	60	60	60	60	60	60	60	60	60	60	60	60
Concentration in °Baumé . .	10	10	10	10	10	10	10	10	10	10	10	10
Duration of pickling in minutes .	2½	2½	3½	3½	3	3	5	5	14	14	20	20
Weight of the disc after pickling, gr.	30·980	31·135	31·906	32·150	30·638	32·495	30·428	32·841	24·801	27·480	30·012	28·009
Loss in weight, . . . gr.	0·658	0·825	0·331	0·374	1·576	0·791	0·732	0·932	6·093	4·728	3·748	3·772
Loss in weight, . . per cent.	2·1	2·5	1	1	5·4	2·3	2·3	2·7	19·5	14·6	11·1	11·8

For unheated sheet iron, the principal loss per 100 sq. cm. of surface amounted from 0·16 to 0·35 g.

The higher the temperature to which the sheet-steel utensil is heated in the muffle-furnace before pickling, the greater the increase in its weight (by oxidation of the surface). As a rule the most favourable average temperature for heating to redness should lie between 650° to 750° C. Below this temperature the combustion of the adhering grease or of the soap solution (proceeding from the manufacture of the rough wares) is incomplete. Moreover, the steel below 600° C. does not preserve that softness necessary for the subsequent enamelling process. The stamped, pressed, and planed rough iron-ware also loses a part of its original suppleness during the course of these operations.

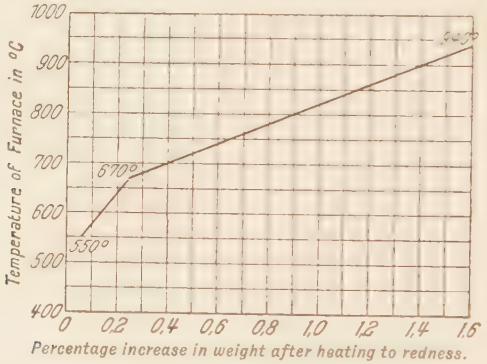

DIAGRAM I.—The increase in weight of the sheet steel after heating is dependent upon the temperature of the furnace.

Further experiments have shown that overstepping the temperature named has a disastrous effect upon the softness and the subsequent loss in the acid pickle, similar to that of exceeding the duration of heating at a medium furnace temperature. In other words, a sheet-iron article heated at 990° C. for three minutes, and pickled in hydrochloric acid of 10° Bé., gives an appreciable metallic loss (14 to 20 per cent.), while the same object heated at 670° C. for the double period (six minutes) and afterwards pickled in the same acid only exhibits 3 to 4 per cent. metallic loss, *i.e.* almost the same amount as sheet iron heated for only three minutes at 670° C. Hand in hand with the higher temperature, *i.e.* with the same overstepping, goes an appreciable extension of the period necessary for the subsequent pickling process. Accordingly, for a rational heating and pickling it is more expedient to increase the duration

of heating at the middle furnace heat (670° C.) when necessary, than to elevate the furnace temperature.

Diagram 2 shows that only three minutes are necessary for pickling (with hydrochloric acid of 10° Bé.) a sheet-iron disc which has been heated at 670° C., while fourteen minutes are required by one heated at 940° C. Pickled under the same conditions in sulphuric acid of 10° Bé. and at 60° C., the period is lengthened in consequence of the greater acid dilution.

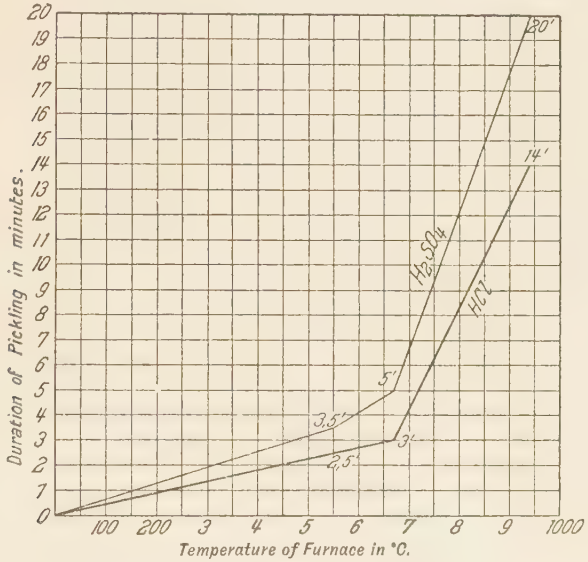

DIAGRAM 2.—Duration in minutes of pickling with hydrochloric and sulphuric acids of 10° Bé.

Diagram 3 shows the influence of the temperature of heating upon the metallic loss after pickling in hydrochloric and sulphuric acids of 10° Bé. and 16° C. Here also the metallic loss grows with rising heating temperature and with increasing acid concentration.

The proportion of hydrochloric acid of 10° Bé. to sulphuric acid of 10° Bé., informs us that the attacking activity upon iron (pickling) of H_2SO_4 : HCl = about 10 : 17 for objects which have been heated above 600° C. before pickling. For iron wares which have been heated below 600° C., the ratio of the attacking and solvent action of H_2SO_4 to HCl stands at about 10 : 22.[1]

[1] According to W. Krämer, 1 : 2 3; compare *Stahl und Eisen*, 1910, vol. xxix. p. 1079, and vol. xxx. p. 1443.

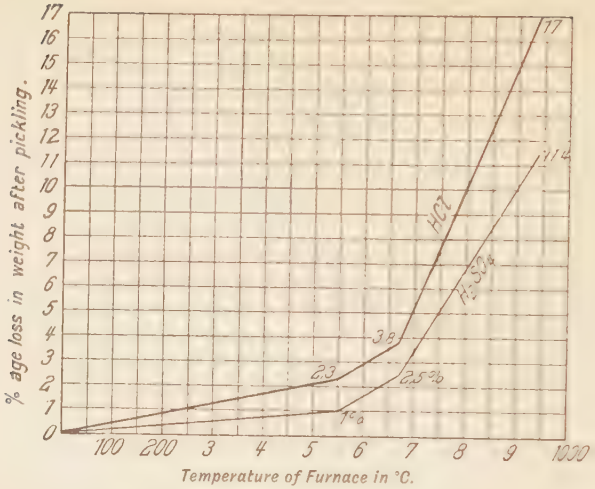

DIAGRAM 3.—Influence of the heating temperature upon the metallic loss after pickling. Curve of the metallic loss after heating at 550°, 670°, or 940° C., and after pickling in hydrochloric or sulphuric acid of 10° Bé. and 60° C.

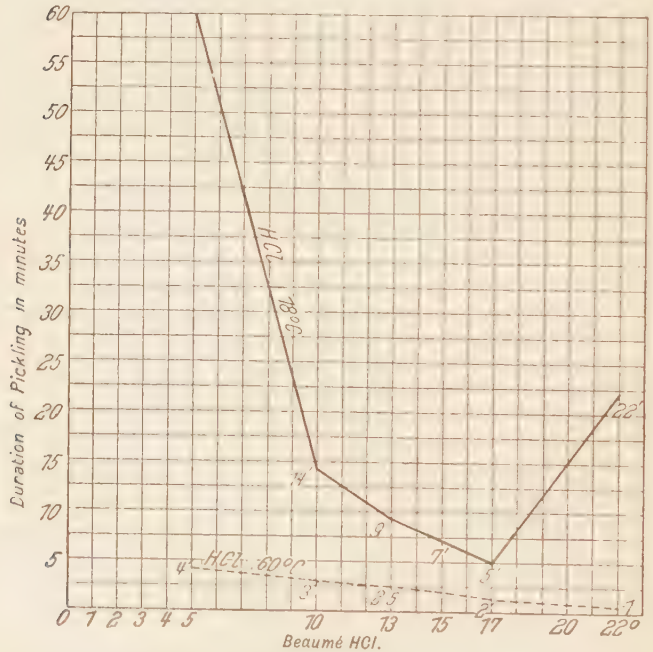

DIAGRAM 4.—The relationship between the pickling period in minutes and the concentration of the hydrochloric acid.
(*a*) at 10° C. (*b*) at 60° C.

The most favourable concentration for (*a*) 17° Bé.
" " " (*b*) 22° Bé.

The superiority of sulphuric acid as a pickling liquid is without question, since sulphuric acid of 60° to 66° Bé. may be produced while the maximum concentration of hydrochloric acid only amounts to 24° Bé. With a price relationship for H_2SO_4 : HCl of 10 : 8 prevailing in many countries, the superiority of sulphuric acid becomes still more pronounced. Further, I have carried out some comparison experiments in order to determine the ratio of the pickling period to the concentration of the acid, *i.e.* to find out the most favourable acid concentration. A pickling bath temperature of 60° C. was thereby established as fundamental. The investigation was first carried out for hydrochloric acid only; the most favourable concentration of hydrochloric acid for pickling purposes at 18° C. lies at 17° Bé.; for heated acid (60° C.) the best concentration lies at 22° Bé.

From numerical Table III. the influence of the heating temperature upon the metallic loss and the duration of pickling may be seen. The experimental series 13 to 18 was performed throughout with sulphuric acid of 7° Bé. and at 60° C. The metallic loss after pickling rose from 1·25 per cent. to 14 per cent., and the necessary pickling period from twenty-five to forty minutes.

Finally, I have added a further Table IV., which gives the results of pickling experiments upon sheet steel not previously heated, *i.e.* upon Martin flux sheet steel which was pickled in the condition it emerged from the ironworks. These experimental sheets were pickled for sixty minutes in sulphuric acid of 10° Bé. The metallic loss in these cases was small, and varied between 0·3 and 0·7 per cent.

TABLE II.—With Diagram 4.

Pickling Experiment with Hydrochloric Acid of Rising Concentration.

(*a.*) Pickled in the cold at 18° C.							
Concentration of the acid . .	5°	10°	13°	15°	17°	22° Bé.	
Pickling period in minutes . .	60	14	9	7	5	22	
(*b.*) Pickled hot at 60° C.							
Concentration of the acid . .	5°	10°	13°	15°	17°	22° Bé.	
Pickling period in minutes . .	4	8	2·5	2	1·5	1	

TABLE III.

Pickling Experiments in a Sulphuric Acid Bath of 7° Bé. and 60° C.

Sheet Iron Heated	(*a*) at 670° C.			(*b*) at 940° C.		
Number of Experiment	13	14	15	16	17	18
Weight of the metallic disc before heating and pickling, gr.	36·890	37·020	42·650	42·223	42·679	43·286
Duration of furnace heating in minutes	3	3	3	3	3	3
Temperature of the furnace in °C	670	670	670	940	940	940
Weight after heating	36·920	37·090	42·736	42·710	43·300	43·705
Increase in weight after heating, gr.	0·030	0·070	0·086	0·487	0·621	0·419
Increase in weight after heating, per cent.	0·08	0·19	0·2	1·1	1·4	0·9
The pickle acid used	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Temperature of the pickling bath in °C.	60	60	60	60	60	60
Concentration of the acid in °Baumé	7	7	7	7	7	7
Weight after pickling, gr.	36·360	36·630	42·261	36 890	37·020	38·311
Loss in weight after pickling, gr.	0·560	0·460	0·475	5·826	6·280	5·394
Loss in weight after pickling, per cent.	1·5	1·25	1·11	13·5	14·5	12·4
		a			*b*	
Duration of pickling in minutes	25	25	25	43	45	40

TABLE IV.

Number of Experiment	19	20	21	22	23	24
Weight of the unheated metallic disc before pickling, gr.	40·250	42·800	30·638	32·495	30·428	32·841
The pickle acid	H_2SO_4	H_2SO_4	HCl	HCl	H_2SO_4	H_2SO_4
Concentration in °Baumé	10	10	10	10	10	10
Temperature of the bath in °C.	60	60	60	60	60	60
Weight after pickling, gr.	40·130	42·650	30·495	32·267	30·377	30·792
Metallic loss after pickling, gr.	0·120	0·150	0·143	0·228	0·051	0·049
Metallic loss after pickling, per cent.	0·3	0·35	0·46	0·68	0·16	0·15
Duration of pickling in minutes	60	60	60	60	60	60
Pickling loss in gr. per 100 sq. cm. surface	0·16 to 0·35 gr.					

In conclusion, there still remains a matter of interest to be mentioned; according to the experiments of my colleague, the presence of small quantities of arsenic is of influence in the pickling process. After adding 1 mg. of sodium arsenate to 1 litre sulphuric acid of 10° Bé., a strongly-heated sheet disc was pickled therein, and after pickling gave a metallic loss of 0·5 per cent. A disc heated under the same conditions was likewise pickled in sulphuric acid of 10° Bé., but without addition of arsenic, and gave a metallic loss of 11 per cent. In the first case only the black iron oxide layer was dissolved away, the metallic iron beneath having been unattacked even after several hours' activity. Burgess has already proved that in presence of arsenic the action of sulphuric acid upon iron is retarded, while before him other investigators had recognised the rust-protecting properties of certain salts, especially those containing arsenic.

Electrolytic Pickling.—There still remains to be discussed the extremely interesting work of C. J. Reed[1] with respect to electrolytic pickling. We have repeated his work in the laboratory. While from want of suitable equipment and from lack of time we have not arrived at the same sensational results as he, yet the idea of an electrolytic acid pickle for sheet steel and articles made from it, deserves the fullest attention and most zealous study. (It must be distinguished from the electrolytic scouring of metallic vessels previous to pickling or zincing.) In contrast to ordinary electrolytic pickling, in which the iron article is suspended as anode in a bath of sodium chloride or sodium sulphate, the Reed method removed the disadvantage inherent therein, viz. that iron by absorption of hydrogen has its properties unfavourably influenced (resistance and elasticity).

Reed started with the fact that the higher oxides are dissolved from the kathode and deposited on the anode, just as metals are dissolved from the anode and deposited on the kathode. Further, he referred to the solubility of black iron oxide in sulphuric acid, which with the customary pickling agents signifies a waste of acid. At a lower temperature and in a more dilute solution, the skin of magnetic iron oxide is dissolved from the kathode side, but only very slowly and with a feeble current. Reed proposes, therefore, a sulphuric acid bath of specific gravity 1·25 (28°·8 Bé.) and a temperature of 60° C., with current of 70 ampères per cubic foot (0·075 amp. per sq. cm.). The solution of the oxide layer now

[1] *Transactions of the American Electrochemical Society*, 1907, xi. pp. 181–183.

takes place rapidly without the metal being chemically attacked. According to Reed, the thickest oxide crust dissolves in two to three minutes. Depending on the thickness of the oxide layer, sheet steel may be pickled in twenty, forty, or eighty seconds. Our own experiments, which were incomplete, however, gave now and then an appreciably accelerated pickling action when using a bath of 30° Bé. sulphuric acid at 60° C., and a current of 7 to 9 ampères per 10 cm. of sheet-iron surface (carbon anodes): the black oxide layer, however, did not dissolve away, but large pieces were simply detached. Individual objects could be pickled in one to two minutes. As a matter of fact we found that similar articles placed in the same bath, but without applying the current, were also beautifully pickled in four to six minutes. We had to contend with deficient current, however, and it is probable that by employing a stronger current our results might have been more favourable.

An iron-ware factory, *e.g.* an enamel works, which prepares about 5000 kg. of rough wares having an average thickness of 0·4 mm., *i.e.* 3200 sq. m. of sheet iron, requires therefore, if the results communicated by Reed are correct, 2,400,000 ampères for two minutes daily, or 8000 ampères during a ten-hours day. At all events a very cheap current supply must be at hand to ensure the process being profitable. That the Reed method might have manifold advantages in store with respect to acid consumption, etc., admits of scarcely any doubt. The process itself allows for the production of the necessary sulphuric acid, in that sulphur dioxide, formed by the combustion of sulphur or pyrites, be supplied at the anode. A further advantage may lie therein, viz. that the iron sulphate could be recovered in a pure concentrated condition by the kathode process. As soon as the electrolyte is saturated with iron sulphate, the pickling liquid need only be allowed to cool in order to obtain the iron sulphate crystals. If much promise be hereby held out for the future, the idea of J. C. Reed deserves the fullest attention and further experiments on the lines indicated in his work.

Although not strictly belonging to this place, the increasing success of the electrolyte scouring processes for objects about to be galvanised deserves mention. One of the recent methods consists in making as kathode the object to be scoured, and as electrolyte a sufficiently concentrated solution of caustic potash or soda to which from time to time small quantities of potassium cyanide

were added. The latter reduces a portion of the oxygen liberated at the anode, thereby diminishing the oxidising tendency in the bath. The process is carried out at a temperature near the boiling-point, and with 4 to 8 volts. The alkali forming at the anode brings about a saponification of the grease upon the metallic object serving as anode. The hydrogen developed exerts at the same time a mechanical action, since it loosens the saponified layer and works it to the surface of the bath. The operation should only last a few minutes.

It appears from the latest researches upon the relationship between the occluded gases and the quality of the steel, that the critical temperature for heating steel and iron has a definite connection with the occluded gases, these consisting of carbon dioxide, carbon monoxide, hydrogen, and nitrogen. Dr G. Belloc [1] has made an interesting study of this subject. He determined the rate of cooling of steel at falling temperatures, and established the following data:—

TABLE V.

Temperature.	Coefficient of Cooling (in tenths of a millimetre).	Observation.
900	−3	Belloc carried out this investigation using the Roberts-Austen differential method. Two masses as near identical as possible were prepared, on the one hand, from the steel to be investigated, and, on the other, from a metal such as copper or platinum. In the interiors of these masses were placed the junctions of two of Le Chatelier's thermo-elements (platinum-rhodium). By connecting both platinum parts with a very sensitive galvanometer, the latter will be brought into relationship with the temperature changes of both junctions.
880	−1	
870	+1	
860	+7	
850	+42	
800	+61	
780	+64	
750	+58	
720	+45	
710	+78	
700	+64	
650	+27	
600	+17	
560	+17	
550	0	
520	+1	
500	+2	
450	+3	
400	+4	

In consequence of the unequal conductivity for heat of both metals, when both masses are heated a temperature difference results which is evidenced by a kick of the galvanometer. This

[1] *Bulletin de la Soc. d'Encouragement*, 1908, April, p. 492.

difference, and therefore also this temperature change, will be more pronounced the greater the velocity of heating, and conversely. We can therefore measure the velocity in question by this method, assuming that both metals undergo no allotropic change. At the maximum heat of the furnace the index of the galvanometer points to 0. On cooling, however, the pointer will kick in the opposite direction. Between 640° and 570° the galvanometer performs a series of oscillating movements, which are a sign of molecular action in the interior of the body, and which in a remarkable way coincide with the maximum exit of gas from the steel. The real maximum of change on cooling appears to lie at 710° C. This temperature, however, according to practical experiments, is a very favourable heating temperature (670° to 710° C.); the idea therefore suggests itself of bringing the physical changes which the steel undergoes on heating into relationship with the nascent state of definite amounts of occluded gas. Carbon dioxide and hydrogen escape first of all (up to 550°); the nitrogen begins to leave at 550°. It is thus noticeable that the principal amount of occluded gas is in the interior of the steel mass. I think it useful to have referred at this point to the possibility of a relationship between the critical (*i.e.* the most suitable) heating temperature and the occluded gases, since I am convinced that this subject still offers a wide field of activity to the metallurgist.

CHAPTER X.

THE CALCULATION OF THE CHEMICAL COMPOSITION OF AN ENAMEL FROM THE MIXED RAW MATERIALS.

In consequence of the increasing importance of the enamelling industry during late years, the delicate theme of the scientific side of the subject has received much greater literary attention. Since the breaking of the ban imposed by possessors of secrets and by the empiricism in problems of enamel manufacture, there is a modern tendency prevalent which is all to its advantage. It is also of importance for the enamel expert, who has not been chemically trained, like a works' foreman, etc., to follow the literature relating to his subject. Especially should the latter be in a position to understand aright the chemical compositions ascribed in these publications to the enamels, as well as to follow the most important of the fundamental chemical ideas to be found therein. Several publications should be read for this purpose. Let us not forget that our enamel industry still employs relatively few trained chemists (although an increasing change for the better is to be noted), and the industry, especially in the small works, is carried out by very able practical men, such as foremen enamellers, who would willingly accept advice and information were this offered to them. The chemist, working amid practical conditions, knows how great is the need for explanation among our honest foremen enamellers. The more we concern ourselves with the education of these indispensable fellow-workers and intermediate links between chief and worker, the greater will be the resulting gain for the industry.

The object of the present chapter is to show how the chemical composition of an enamel may be determined by calculation alone. This mode of elucidating chemical composition also renders yeoman service in cases, where, from want of a chemist, or of a laboratory, or still more frequently from lack of time, the fairly complex

TABLE VI.—The Average Chemical Composition of the most

Designation of the Raw Materials.	Chemical Name.	Chemical Formula.
Sodium felspar (Albite) .	Sodium aluminium silicate	$Na_2Al_2Si_6O_{16}$
Norwegian felspar (Orthoclase).	Potassium aluminium silicate.	$K_2Al_2Si_6O_{16}$ $K_2O + Al_2O_3 + 6SiO_2$
Quartz or pure sand . .	Silicic acid anhydride	SiO_2
Fluorspar $\frac{a}{b}$ . . .	Calcium fluoride	CaF_2
Cryolite $\frac{a}{b}$ . . .	Sodium aluminium fluoride	$3NaF + AlF_3$
Sodium silicofluoride $\frac{a}{b}$.	Sodium silicofluoride	$Na_2SiF_6 = 2NaF + SiF_4$
Borax	Sodium tetraborate	$Na_2B_4O_7 + 10H_2O$
Boric acid (Tuscan) . .	Sassoline native boric acid	$B(OH)_3$ or $B_2O_3 + 3H_2O$
Calcined soda . . .	Sodium carbonate	Na_2CO_3
Sodium saltpetre . .	Sodium nitrate	$NaNO_3$
Clay	Aluminium silicate	$Al_2Si_2O_7 + 2H_2O = Al_2O_3 + 2SiO_2 + 2H_2O$
Kaolin from Zettlitz . .	Aluminium silicate	$Al_2Si_2O_7 + 2H_2O = Al_2O_3 + 2SiO_2 + 2H_2O$
Calcspar	Calcium carbonate	$CaCO_3$
Plate glass . . .	An alkaline calcium silicate	Variable

important Enamel Raw Materials expressed in Percentages.

Sodium Oxide (Na_2O).	Potassium Oxide (K_2O).	Calcium Oxide or Lime (CaO).	Magnesium Oxide or Magnesia (MgO).	Barium Oxide or Baryta (BaO).	Iron Oxide (Fe_2O_3).	Cobaltous Oxide (CoO).	Nickel Oxide (Ni_2O_3).	Tin Oxide (SnO_2).	Fluorine (F).	Aluminium Oxide or Alumina (Al_2O_3).
11·79	0–1	0–2	...	...	...	...	...	...	...	19·40
2·40	13·82	0·27		...	0·65	...	...	...	...	18·75
...	...	* Calc.	...	...	...	...	...	...	...	...
...	...	67·79*	...	...	...	...	...	...	32·21	...
...	...	74·70	...	...	...	...	...	...	25·30	...
...	...	...	...	...	...	...	...	...	54·28	...
38·22	...	...	...	...	...	...	...	...	42·67	19·08
...	...	...	...	...	...	...	...	...	60·63	...
26·21	...	...	...	...	...	...	...	...	48·26	...
16·26	...	...	...	...	...	...	...	...	...	...
..	...	...	...	...	...	...	...	...	...	...
58·50	...	...	...	...	...	...	...	...	...	...
36·47	63·53 nitric acid anhydride (N_2O_5)		...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	34·00
...	...	...	...	...	0·70	...	...	...	...	38·67
...	...	56·00	...	...	...	...	...	...	...	...
13·00	13·40	3·40	...	...	...	...	...	...	...	...

TABLE VI.

Designation of the Raw Materials.	Chemical Name.	Chemical Formula.
Sodium felspar (Albite)	Sodium aluminium silicate	$Na_2Al_2Si_6O_{16}$
Norwegian felspar (Orthoclase)	Potassium aluminium silicate	$K_2Al_2Si_6O_{16} = K_2O + Al_2O_3 + 6SiO_2$
Quartz or pure sand	Silicic acid anhydride	SiO_2
Fluorspar $\frac{a}{b}$	Calcium fluoride	CaF_2
Cryolite $\frac{a}{b}$	Sodium aluminium fluoride	$3NaF + AlF_3$
Sodium silicofluoride $\frac{a}{b}$	Sodium silicofluoride	$Na_2SiF_6 = 2NaF + SiF_4$
Borax	Sodium tetraborate	$Na_2B_4O_7 + 10H_2O$
Boric acid (Tuscan)	Sassoline native boric acid	$B(OH)_3$ or $B_2O_3 + 3H_2O$
Calcined soda	Sodium carbonate	Na_2CO_3
Sodium saltpetre	Sodium nitrate	$NaNO_3$
Clay	Aluminium silicate	$Al_2Si_2O_7 + 2H_2O = Al_2O_3 + 2SiO_2 + 2H_2O$
Kaolin from Zettlitz	Aluminium silicate	$Al_2Si_2O_7 + 2H_2O = Al_2O_3 + 2SiO_2 + 2H_2O$
Calcspar	Calcium carbonate	$CaCO_3$
Plate glass	An alkaline calcium silicate	Variable

—*continued.*

Boric Acid Anhydride (B_2O_3).	Carbonic Acid Anhydride or Carbon Dioxide (CO_2).	Silicic Acid Anhydride or Silica (SnO_2).	Sodium Fluoride (NaF).	Aluminium Fluoride (AlF_3).	Sodium (Na).	Aluminium (Al).	Silicon (Si).	Water (H_2O).	Loss on Heating.
...	...	68·81	...	...	...	..	...	...	...
...	...	64·44	...	...	...	...	...	...	...
...	...	100·00	...	...	...	...	...	...	...
...	...	...	...	...	...	...	..	...	...
...	...	...	...	..	...	...	...	...	...
...	...	...	...	...	32·85	12·85	...	...	...
..	...	...	60·00	40·00	...	...	...	...	...
...	...	...	...	...	24·44	...	14·91	...	...
...	...	25·47	...	...	...	...	...	..	...
36·59	...	...	...	...	...	...	...	47·15	...
45·56	...	...	...	...	...	...	...	43·55	...
...	41·50	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...
...	...	53·00	...	...	...	...	...	...	12·00
...	...	46·62	...	...	...	...	...	...	14·30
...	44·00	...	...	...	...	...	...	...	...
...	...	70·20	...	...	...	...	...	...	...

chemical analysis of an enamel cannot be carried out. Naturally the chemical composition of an enamel obtained by calculation alone often deviates a little from the actual composition, but it answers, however, completely for practical requirements.

The mode of calculation is based upon a knowledge of the quantities and method of fixing together the raw materials, as well as upon their average chemical composition, which when of good quality and from a trustworthy source may be regarded as constant. As a rule, enamels are produced by mixing and melting together the following raw materials in definite proportions by weight: borax, boric acid, felspar, quartz, fluorspar, soda, saltpetre, cryolite, clay, cobalt oxide, nickel oxide, limonite, tin oxide, and more seldom calcspar and magnesite. Table VI. gives a summary of the usual chemical composition of these raw materials.

The above are mostly "salts" in the chemical sense of the term, consisting of a "base" and an "acid anhydride."

The basis or base may be:—

Sodium oxide, shortly termed soda, with the chemical formula Na_2O; calcium oxide, known as lime, having the formula CaO; magnesium oxide, or briefly magnesium, represented chemically by MgO; potassium oxide, K_2O; aluminium oxide or alumina, Al_2O_3; barium oxide, BaO.

The acid anhydride in these salts is usually:—

Carbonic acid anhydride, or shortly, carbonic acid of formula CO_2, which is evolved during the melting; nitric acid anhydride of formula N_2O_5, evolved during melting; fluorine, F, which is partially evolved during melting as silicon tetrafluoride (SiF_4); silicic acid anhydride, shortly termed silica, having the formula SiO_2 (silicon dioxide) and non-volatile; boric acid anhydride, or briefly boric acid (boron trioxide), B_2O_3, non-volatile; stannic acid anhydride, tin dioxide or tin oxide, SnO_2, which is very slightly volatile or not at all.

The majority of metallic oxides, such as cobalt oxide, nickel oxide, iron oxide, chromium oxide, manganese superoxide (limonite), zinc oxide, copper oxide, etc., are bases.

By melting these raw materials, most of the salts decompose with evolution of carbon dioxide, nitric acid, hydrofluoric acid, and chlorine. The other acidic anhydrides are either non-volatile or only slightly so. The loss after melting together the mixed raw materials is given accordingly by the sum of the evolved carbonic acid (from the soda and other carbonates), fluorine (from fluorspar and cryolite), nitric acid (from saltpetre), and water of crystallisation

(from borax, etc.), together with the loss due to manipulation (2–5 per cent.).

TABLE VII.

Loss on Melting the Enamel Raw Materials.

Raw Materials.	Mass in kg.	Component Evolved.	Loss on Melting in kg.	Loss on Melting, per cent.
Borax	100	Water	47·20	47·20
Calcined soda	100	Carbonic acid	41·50	41·50
Sodium saltpetre	100	Nitric acid anhydride	63·53	63·53
Clay	100	Water and carbonic acid	12·00	12·00
Kaolin	100	Water and carbonic acid	14·00	14·00
Boric acid	100	Water	43·50	43·50
Calcspar	100	Carbonic acid	44·00	44·00
Cryolite	100	Fluorine (as SiF_4)	20·00	20·00
Fluorspar	100	Fluorine (as SiF_4)	8·00	8·00

The majority of the remaining raw materials undergo no essential loss on melting, since at an extremely high temperature only partial volatilisation can take place at the most (tin oxide).

Setting out from these two tables we proceed to the real exercise, namely, the calculation of the chemical composition of an enamel from a knowledge of the amounts of raw materials mixed together.

As an example, let us take a white enamel, designated C, whose recipe runs as follows:—

TABLE VIII.

Raw Material.	Chemical Formula.	Weight in kg.	Weight, per cent.
Borax	$Na_2B_4O_7+10H_2O$	30·00	30·00
Felspar	$K_2O+Al_2O_3+6SiO_2$	30·00	30·00
Quartz	SiO_2	17·00	17·00
Cryolite	$3NaF+AlF_3$	11·90	11·90
Calcined soda	Na_2CO_3	3·92	3·92
Sodium saltpetre	$NaNO_3$	2·21	2·21
Fluorspar	CaF_2	1·97	1·97
Clay	$Al_2O_3+2SiO_2+2H_2O$	3·00	3·00
	Total	100·00	100·00

How do the weight relations change in this crude mixture C after melting?

The loss on melting which takes place is easy to calculate from Table VII.

TABLE IX.—*The White enamel* C *after the melting process.*

	a.	*b*	*c.*	*d.*	*e.*
	Weight in kg. before Melting.	Percentage Loss on Melting.	Loss on Melting in kg.	Weight in kg. after subtracting the Loss on Melting.	Percentage Weight after Melting.
Borax . . .	30·00	47·20	14·16	15·84	19·80[1]
Felspar . . .	30·00	...	...	30·00	37·60
Quartz . . .	17·00	...	...	17·00	21·30
Cryolite . . .	12·00	20·00	2·40	9·60	12·00
Calcined soda . .	4·00	41·50	1·70	2·30	2·80
Sodium saltpetre .	2·30	63·53	1·46	0·84	1·00
Fluorspar . .	2·00	8·00	0·16	1·84	2·20
Clay . . .	3·20	12·00	0·38	2·82	3·30
Total .	100·50	...	20·26	80·24	100·00

According to Table IX. the calculated loss on melting for this enamel is 20·26 per cent. In practice the small loss on manipulation must often be increased.

After establishing by calculation the weight relations of the raw materials after melting from Table IX., we proceed to analyse every one of these raw materials into its chemical components, *i.e.* into bases (Na_2O, K_2O, CaO, etc.), and non-volatile acid anhydrides (SiO_2, B_2O_3, F, etc.), using Table VI. for calculating the percentage composition of the individual raw materials. The like components of all the raw materials, *e.g.* the silica (SiO_2), proceeding from felspar, quartz, and clay, will afterwards be added and the chemical composition given to the enamel.

Table X. now brings us near our goal. Therein we have analysed the individual amounts of the raw materials into the corresponding components, using Table VI. for the usual percentage compositions of the same.

If we have 30 kg. borax in the crude enamel mixture, this amount corresponds to—

Na_2O (soda)	4·86 kg.
B_2O_3 (boric acid anhydride) . .	10·98 „
H_2O (water of crystallisation) . .	14·16 „
Total .	30·00 kg.

[1] Example of the calculation :—*e.g.*, $19{\cdot}80 = \frac{15{\cdot}84 \times 100}{80{\cdot}24}$.

TABLE X.

Analysis of the Raw Materials into their Components after Subtracting the Loss on Melting (Table IX, *c.*)

With the aid of Table VI.

	Percentage Amounts according to Table IX, *a.*	Percentage Chemical Composition according to Table VI.	Sodium Oxide (Na_2O).	Potassium Oxide (K_2O).	Lime (CaO).	Magnesia (MgO).	Iron Oxide (Fe_2O_3).	Alumina (Al_2O_3).	Silica (SiO_2).	Boric Acid (B_2O_3).	Fluorine (F).	Nitric Acid (N_2O_5).	Water (H_2O).	Carbonic Acid (CO_2).	Loss on Heating.
			kg.	kg.	kg.	kg.	kg.	kg.	kg.	kg.	kg.	kg.	kg.	kg.	kg.
Borax . . .	30·00	16·26 Na_2O, 36·59 B_2O_3, 47·15 H_2O	4·86	...	...	...	...	...	...	10·98	...	...	14·16	...	...
Felspar . .	30·00	2·4 Na_2O, 13·8 K_2O, 0·27 CaO + MgO, 0·65 Fe_2O_3, 18·75 Al_2O_3, 64·44 SiO_2	0·72	4·10	0·03	0·03	0·20	5·62	19·30	...	...	...	...	...	...
Quartz . .	17·00	100·00 SiO_2	...	...	...	...	...	...	17·00	...	...	...	...	...	...
Cryolite * . .	11·90	38·22 Na_2O, 42·67 F, 19·08 Al_2O_3	4·58	...	...	...	...	2·22	...	...	5·10	...	...	...	...
Calcined soda .	3·92	58·5 Na_2O, 41·5 CO_2	2·32	...	...	...	...	...	...	...	...	...	...	1·60	...
Sodium saltpetre .	2·21	36·47 Na_2O, 63·53 N_2O_5	0·81	...	...	...	...	...	...	...	...	1·40	...	...	...
Fluorspar * . .	1·97	74·7 CaO, 25·3 F	..	...	1·47	...	...	...	...	...	0·50	...	...	...	...
Clay . . .	3·00	34·00 Al_2O_3, 53·00 SiO_2, 12·00 Loss on Heating	...	...	...	...	...	1·00	1·70	...	...	...	...	...	0·30
Total . .	100·00	...	13·29	4·10	1·50	0·03	0·20	8·84	38·00	10·98	5·60	1·40	14·16	1·60	0·30

* The composition was calculated upon Na_2O and CaO instead of Na and Ca, in order to facilitate the later addition of the bases, since the analytical results are expressed in terms of oxides of the elements.

We see, however, from Table VI. that borax in general consists of—

Na_2O	16·26 per cent.
B_2O_3	36·59 „
H_2O	47·15 „

By multiplying 30 and 16·26 together and then dividing by 100, we obtain the amount of sodium oxide in 30 kg. borax. In this way the calculation was made for every substance in Table X. (p. 93).

Let us now collect the results from Table X. into a new Table XI.; for 100 kg. of unmelted raw enamel, the following chemical composition is given:—

TABLE XI.

Chemical Composition of the Crude Enamel A.

Na_2O (sodium oxide)	13·29 per cent.
K_2O (potassium oxide)	4·10 „
CaO (lime)	1·50 „
MgO (magnesia)	0·03 „
Fe_2O_3 (iron oxide)	0·20 „
Al_2O_3 (alumina)	8·84 „
SiO_2 (silica)	38·00 „
B_2O_3 (boric acid anhydride)	10·98 „
F (fluorine)	5·60 „
N_2O_5 (nitric acid anhydride)	1·40 „
H_2O (water)	14·16 „
CO_2 (carbonic acid)	1·60 „
Loss on heating	0·30 „
Total	100·00 per cent.

On melting this enamel there are evolved carbonic acid, water, the loss on heating, nitric acid anhydride, and a part of the fluorine which combines with the silicon of the silica to form volatile silicon fluoride[1] (SiF_4). There remains, therefore, after melting the raw material, a finished enamel of the following composition:—

[1] Only about a third of the total fluorine is evolved on melting. The view held by some experts that fluorine is completely evolved, is untenable.

TABLE XII.

Composition of the Finished Enamel.

Na_2O	13·30 kg.	
K_2O	4·10 „	
CaO	1·50 „	
MgO	0·04 „	
Fe_2O_3	0·20 „	
Al_2O_3	5·62 „	
SiO	38·00 „	− 1·54 =
B_2O_3	10·98 „	36·46 kg.
F_2	3·72 „	

We may assume that about a third of the fluorine from the cryolite $= \frac{5·10}{3} = 1·70$ and a fourth from the fluorspar $= \frac{0·50}{4} = 0·12$, *i.e.* a total of 1·82 kg. of fluorine is evolved as silicon fluoride. A small loss of SiO_2 is also occasioned, which furnishes the necessary amount of silicon (Si) for the formation of the volatile silicon fluoride (SiF_4). This quantity of silicon is calculated as follows:— $Si : F_4 = 28 : 4 \times 19 = 28 : 76 = x : 1·82$ fluorine; $x = 0·72$, therefore the amount 1·82 of fluorine loss requires 0·72 Si for the formation of volatile silicon fluoride.

To what amount of SiO_2 (silica) does 0·72 Si correspond?

$SiO_2 : Si =$ molecular weight of silica : atomic weight of silicon

$= (28 + 32) : 28 = 60 : 28 = x : 0·72.$

$x = 1·54$ SiO_2 (silica). Therefore there only remains 36·46 SiO_2; hence after melting the composition is:—

TABLE XIII.

Na_2O	13·30 kg.
K_2O	4·10 „
CaO_2	1·50 „
MgO	0·04 „
Fe_2O_3	0·20 „
Al_2O_3	5·62 „
SiO_2	36·46 „
B_2O_3	10·98 „
F_2	3·72 „
Total	75·92 kg.

If this composition be calculated upon 100 kg., *i.e.* in percentages, we have the final:—

TABLE XIV.

Na_2O	17·51 per cent.
K_2O	5·40 „
CaO	1·97 „
MgO	0·05 „
Fe_2O_3	0·26 „
Al_2O_3	7·41 „
SiO_2	48·03 „
B_2O_3	14·46 „
F_2	4·91 „
Total	100·00 per cent.

In our case we have to deal with an easily fusible white culinary enamel, resulting from the relatively large amounts of boric acid and alkali and a silica content of only 48 per cent.

The chemical composition of a ceramic product is also frequently expressed in a molecular formula. Although in actual practice the molecular formula finds little use in the enamel manufacture, yet it is necessary to show here how the above percentage chemical composition can be expressed in a molecular formula. The molecular formula gives the number of molecules of the separate components (bases and acidic anhydrides) which are contained in an enamel. As already mentioned, the bases considered are the oxides of the alkalies (K, Na), and alkaline earths (Ca, Ba), while the acids are silica, fluorine, boric acid anhydride and tin oxide (on account of the formation of stannic acid salts, or stannates), both being united by alumina (Al_2O_3), which stands as the connecting link between bases and acids. The molecular formula is constructed in such a way that the sum of the base molecules amounts to 1.

From the given weights (Table XIV.) of the enamel components, we calculate the number of molecules of the same, since the weight is multiplied by the molecular weight of the components; *e.g.*, 17·51 kg. Na_2O : molecular weight of Na_2O $(=62) = 17{\cdot}51 : 62 = 0{\cdot}282$ Na_2O, *i.e.* about $\frac{1}{3}$rd of a molecule of Na_2O.

Based upon the following known molecular weights of

$Na_2O = 61$;	$MgO = 40$;	$SiO_2 = 60$;
$K_2O = 94$;	$Fe_2O_3 = 160$;	$B_2O_3 = 70$;
$CaO = 56$;	$Al_2O_3 = 102$;	$F_2 = 38$;

the molecular formula is calculated from XIV. as follows:—

TABLE XV.

Na_2O	0·282			SiO_2	0·800
K_2O	0·057			B_2O_3	0·206
CaO	0·035	Al_2O_3	0·072	F	0·129
MgO	0·001				
Fe_2O_3	0·002				
	0·377				

The left-hand sum for the bases or radicals (RO) gives 0·377. In order to deduce the formula so that the sum of the bases is equal to 1, we must multiply the figures by the factor $1 : 0{\cdot}377 = 2{\cdot}65$ and thereby obtain the customary molecular formula:—

TABLE XVI.

Na_2O	0·747			SiO_2	2·120
K_2O_2	0·152			B_2O_3	0·546
CaO	0·093	Al_2O_3	0·191	F_2	0·342
MgO	0·003				
Fe_2O_3	0·005				
	1·000				

CHAPTER XI.

ON THE TECHNOLOGICAL HISTORY OF TINNING.

In a previous chapter I have sought to give a short history of the development of enamelling technology. Most of the present-day enamelling works possess a department occupied with the manufacture of all kinds of tinned utensils for the house, kitchen, and hospital.

Tinned ware still retains the patronage of a large section of the public, especially so as tin is numbered among the absolutely innocuous, easily-worked metals, and finds important use particularly for army equipment, the preserve industry, etc., in spite of the momentary tendency to make military utensils from aluminium. Originally serving for the production of ornamental articles such as warlike implements, headgear, and incrusted silver articles, tin became of extraordinary importance for antique bronze, and for the preparation of various kinds of bronze objects. Hand in hand with the later application for tinning copper and iron went the use of pure tin in the form of cast or chased jugs, vases, plates, dishes, etc. This use lasted until our time, and some years ago received an artistic application in a fresh direction [1] (Kaiser tin).

How many valuable artistic vessels made of tin must have been melted up during the last ten years in order to become saleable owing to the extraordinary rise in the price of tin for trade and industrial purposes! From the weak layer of tin upon antique vessels, it appeared as if the tinning process in earlier times had been carried out at a higher temperature than at present; as a matter of fact, the tin was distributed uniformly throughout in very thin layers by means of a fine brush. Originally, only ornamental objects of copper or bronze were tinned, while later

[1] The tinned objects of antiquity have become modern once more. Most of such artistic work, however, is of later date. In order to simulate the appearance of "antique tin," the object to be rendered antique is dipped into a solution of alum to which a few drops of hydrochloric or sulphuric acid have been added.

the process was applied to copper house utensils, and still later to those of iron.

We have already dealt in some degree with the older German tinning industry. At first tinning was practised in Germany as an auxiliary branch of various handicrafts, such as that of the coppersmith, tinner, spur-maker, etc., and only later came its complete separation as an individual industry. Nuremberg was the centre of the tinning industry when this was regarded as an independent trade, and practised quite apart from the above-named crafts. This [1] may be gathered from an interesting account by Weigel on tinning in Germany before the end of the seventeenth century.

To-day, in places where the tinning industry is established, the process of tinning is one which belongs almost of necessity to several trades; *e.g.*, the coppersmith tins his copper utensils, the tinner his cases, strainers, ladles, and kitchen equipment made of black sheet metal, the spurrier his bars, stirrups, spurs, and horse combs, the locksmith his locks, bars and handles, and the compass-smith innumerable articles for his handicraft. Nevertheless, in Nuremberg especially, and elsewhere, firms are found which are supported almost entirely by tinning alone, making a speciality of it, and thereby acquiring the fame which is well known to be associated with it. These firms, however, only tin work already finished and turned out by various industries. On the other hand, in the electorates of Saxony and Brandenburg, where tough iron is mined, also in Milan and other places, there are found many tinners who are accustomed to tin wrought sheet iron in large quantities for the tinner and other trades which work up white sheet iron; such sheets, however, must be of tough iron, since brittle steel cannot be tinned satisfactorily.[2]

All iron intended for tinning must first be pickled, then scoured and made as clean as possible, for where the smallest impurity remains no tin will adhere. It is next tinned and cleaned anew, so as to acquire a beautiful polish. In order, however, that a proper artistic effect may be produced, the tin must be well purified, whether it be a so-called S-iron, roll or standard tin, and fused;

[1] Appeared in the *Illustr. Zeitung für Blechindustrie*, Leipzig, 1908.

[2] One usually accepts the year 1510 as the beginning of tinned sheet iron manufacture. In a singular way, however, documents were found in the Asylum of St Thomas at Andernach dating from the year 1261, which had been preserved in a box of tinned iron. The box was closed with a seal and in good condition. In the Saxon Erzgebirge, sheet iron had been tinned before the process was introduced into England. Large modern works for the manufacture of tinned sheet iron in England were founded in 1860 by John Saunders at Kidderminster, and by Edward Monewood at Llanelly.

here special skill in manipulation is required in order that it may be well applied, and also that the iron may readily accept the tin. In performing the operation the work must not soon become black or rough and gritty, but retain a beautiful smooth coat possessing a brilliant lustre and reflective power.

The usefulness of this craft not only lies in the fact that black iron acquires a beautiful lustre, but also that it is protected from rust, while copper is preserved against verdigris, consequently the tinned utensils made from the above metals may find manifold use in a place like the kitchen, being employed with advantage where the pure metals would prove injurious.[1]

I have quoted Weigel literally, because the description of tinning is given correctly and in a characteristic manner, and because we are able to gather therefrom the extent to which the tinning of house utensils, as well as the preparation of tinned sheet iron, had developed about the seventeenth century. In the work quoted, we also find a woodcut which shows us the workshop of a German tinner about the same period. A small tinning furnace and several tubs for the scouring water constitute the most important implements therein. The picture is accompanied by the following allegory:—

"Das von dem Feuer erweichte Zinn
verschmäht nicht Kupfer oder Eisen.
So will der Lieb'-erhitzte Sinn
nicht Freund noch Feinde von sich weisen:
Er teilet mit, so viel er kann,
und rühmet nie, was er getan."

The history of the development of tinning technique in France is very instructive. It appears as if the preparation of tinned sheet on a commercial scale first took place about the year 1726. The real development of tinning, however, went hand in hand with the increasing knowledge of pickling processes, with the production of mineral acids, and with the progress made in iron

[1] References to literature of interest; Joot Amman, *A proper description of all the world's occupations, high and low, spiritual and temporal, and of all arts, crafts, and commerce from the largest to the least, also upon their origin, invention, and uses. Very carefully described and written to suit German readers, by the famous Hans Sachs; the book is very useful and pleasant to read, being also illustrated by original diagrams which should be of special service to all artists and professional men.* The book appeared in 1568 at S. Feierabend near Frankfort a-Main (Nuremberg Public Library). Compare an article in the *Illustr. Ztg. für Blechindustrie*, Leipzig, No. 42 (1910), p. 2544.

Further, F. M. Feldhaus, "Antique Soldering Technology" ("Die alte Löttechnik"), *Chem. Ztg*, No. 127 (1910), p. 1133; and *Piazzi Universalle* of Thomas Garzani, 1619. Published by Lukas Tennis (Royal Public Library at Munich).

and sheet-steel manufacture. That sheet iron previous to tinning must be carefully freed from the adhering oxide layer by pickling in acids, is a well-known fact.

It is well worth the trouble to deal more intimately at this point with the position of this technology towards the end of the eighteenth and at the beginning of the nineteenth century. In some works the sheet iron to be tinned is dipped in sal-ammoniac solution, next heated in a special furnace to a red heat, and then, while red hot, dipped into water. The layer of magnetic oxide of iron easily falls off after this treatment. Eventually the process was improved by hammering and beating, with the object of shortening the succeeding pickling process. Immersion in sal-ammoniac solution before heating, has the effect of causing the nascent ammonia and a part of the hydrogen to penetrate between the oxide layer and the metal, the former being thus lifted off mechanically by gas pressure. In addition, the different rates of contraction of the oxide layer and the sheet metal on cooling, produce a partial loosening of the former. On the other hand, a part of the chloride is fixed as hydrochloric acid on the iron surface, and by subsequent immersion in water accelerates the chemical solution of the magnetic iron-oxide layer.

Originally the pickling was performed with organic acids. In one case an acetic acid bath was used in which about 4 lb. 2 oz. of sal-ammoniac were dissolved. In another case, for the same purpose, oxalic acid, lactic acid, etc., were used, the latter being produced by the fermentation of organic substances. The advantage afforded by warm pickling agents was known, since the observation had been made that sheet iron was more quickly pickled when the temperature of the acid bath was raised. In Germany the so-called vegetable acids, or the "Sicherwasser," were often used, the latter being prepared by the fermentation of meal. Every tinnery boasted upon the excellence of its pickling agents, as do many branches of manufacture at the present time.

The preparation of pickling agents formed a very strictly-protected works' secret. One sought to shorten the duration of pickling by scraping the sheet iron with clay fragments, or rubbing it with sand before immersion in the acid. It cannot be overlooked that, corresponding to the feebly acidic character of the acids employed, the pickling was a very tedious operation, especially when we see the duration of pickling reduced to thirty or forty minutes in a modern plant. It was none less than the famous French

chemist and physicist Réaumur, who was occupied with this problem during the period named, and who first recommended dilute sulphuric acid for pickling sheet iron before tinning.

Leonhardi, again, prefers a pickle prepared by allowing chestnut meal to ferment, this being a luxury only possible in specially privileged districts. Rimmann[1] employed poor milk, spent grain, or acidified potato paste which were fermented. Gmelin[2] proposed the acid water obtained by the distillation of peat (Holzessig).

In the year 1725 Réaumur communicated the results of his pickling experiments to the French Academy of Sciences. Among other things he proposed to immerse the sheet iron in vinegar, then to take it out and expose it to atmospheric action. He found that the sheet iron so treated was completely pickled within forty-eight hours after six to eight immersions.

What progress has been attained in the meantime with our modern sheet-iron pickling processes![3] This progress is intimately connected with the commercial preparation and use of sulphuric and hydrochloric acids, and may be shortly discussed at this stage. Angelus Sala, an Italian physician and chemist, who lived, however, in Germany, discovered sulphuric acid by experimenting on the combustion of sulphur in presence of water and oxygen. It was then known as "Schwefelgeist" (*spirits of sulphur*). Although this acid had been known earlier and, in fact, had been employed by the alchemists, its production by the distillation of iron vitriol was very complicated. The French chemists Nicolas Lefèvre and Lemery made a great advance in the production of this acid by the addition of saltpetre, and this at once brought about a revolution in the manufacture of sulphuric acid. The price of the sulphur spirit or "Glockenschwefelol" (*oleum sulfuris per campanam*) sank from thirty-three francs to only six francs per kilogramme. (To-day ninety times the quantity of sulphuric acid is delivered at almost the same price!) In 1746 the Englishmen Roebuck and Garbett improved the process still further, and from now onwards England became the centre of this industry (*English sulphuric acid*); at this time also the production of sulphuric acid developed in the Harz district (termed *Nordhausen* or *fuming sulphuric acid*).

After this necessary deviation, let us turn to our real subject again; the process of pickling sheet iron intended for tinning was in general as follows: Various wooden vats were placed in order containing weaker or stronger acids (according to the degree progressed by the fermentation). The sheet iron was first laid in the vat containing the weakest acid, and then proceeded through

[1] *Eisenkunde.*
[2] *Technische Chemie.*
[3] Julius Grunwald, *Stahl und Eisen*, "On Modern Pickling Agents, the Heating of Sheet Steel, and Recent Methods," 1909.

each in turn to the one holding the strongest acid. The sheet iron was allowed to remain in the separate vats for twenty-four hours. Then it was washed with water, and hand-scrubbed with straw and sand.

In the modern pickling processes the agent is sulphuric acid, while frequently, and immediately before tinning, the sheet iron is laid in dilute hydrochloric acid solution. That the favourable effect of chlorine upon the utensil to be tinned had been known for a long time, we learn from the early use of sal-ammoniac (ammonium chloride). Sal-ammoniac was added to the pickling agent, and also to the actual tinning bath.

Until the revised legal regulations were issued in 1887, lead was generally added to the fused tin, on the one hand for easier tinning, and on the other from motives of gain. The tinning furnaces, as a rule, were installed for about 800 kg. tin. In earlier days 5–8 kg. of *Arcanum*, a known alloy of lead, bismuth, and antimony, were added to 15–18 cwt. of tin, either to increase the lustre, or to depress the fusion point, or to produce a silvery appearance to the tinning. The least of the earlier tinned utensils could furnish evidence for the strict modern regulations as to the addition of lead, antimony, etc. At that time, owing to carelessness, often dangerous amounts of lead were added. Newton proposed the addition of bismuth in order to make the tin more readily fusible.

For preventing the oxidation of the molten tin surface, a specially prepared beef tallow was used in place of the palm-oil grease which is now used. The correct recipe for the preparation of this oxidation preventative was a secret strictly preserved for a long time in some countries. Many such compositions were discovered. The beef tallow was blackened by quickly heating and by the addition of small quantities of soot. Réaumur,[1] to whom our technology owes many suggestions, investigated the influence and mode of working of the different fats or other substances employed in the tinning process, and showed that the part played by the fat was not exhausted in merely preventing oxidation, but that under certain conditions this, like several other substances, promotes the smoothness and uniformity of the tinning in an extraordinary way. He observed that a tin bath, which was already cooled down so far that an iron sheet coated with blackened beef tallow was not tinned further, was still in a condition to tin a sheet covered with resin, that by further lowering of the

[1] *Mémoires de l'Academie des Sciences*, 1725.

temperature the tin bath refused the resin, but that a sheet covered with wax still accepted tin, while with further cooling of the tinning bath an iron sheet powdered with sal-ammoniac could still be tinned. He thereupon drew up a series of the most suitable materials for covering the surface of the tinning bath, beginning with blackened beef-tallow and ending with sal-ammoniac.

To-day zinc chloride is used in many places for the same purpose. Dietrich[1] proposed a mixture of resin and partly burnt beef-tallow. A preserved recipe consisted in melting in a cauldron 20 lb. tallow, adding to it 4 lb. resin, 8 oz. finely powdered sal-ammoniac and 4 oz. of petroleum, the whole being intimately mixed together.

A mixture of clay with dung deserves mention as an original substitute for beef-tallow. Well-purified sand-free loam was mixed with about one-fourth to one-third its weight of dung, forming balls about 8 cm. in diameter; these were allowed to dry, and heated in the oven to a dark red glow, all the apertures being closed air-tight. The mass was allowed to cool in the oven, and to 15 kg. of the powder so obtained, 60 gr. of powdered sal-ammoniac were added. The tinning bath was covered to a thickness of 3–4 cm. with this powder. Unfortunately there is no information to hand on the action of this disagreeable mixture, whose chief value may indeed lie in the sal-ammoniac. From this we see how the search after new resources for the tinning technology was already in evidence at an early date. A tallow melting at a lower temperature and not blackened, is unemployable.

At the beginning of the nineteenth century two varieties of tinned sheet iron were distinguished, viz. one having a dull and the other a brilliantly lustrous surface. The dull species was prepared by using a tinning bath with one-third lead content and small quantities of copper, antimony, and bismuth. Moreover, a small quantity of arsenic sulphide was added to the molten tin. After tinning, the sheets or the sheet-iron objects, even as to-day, were freed from adhering grease by scraping with bran, and finally sanded as finished wares.

It is well known that by tinning with a bath at too high a temperature (over 235° C.), the objects on cooling acquire a yellowish tint. An account dating from the year 1768[2] informs us that at this period it was already understood how to prevent this yellow coloration by dipping (two to three minutes) in a boiling dilute

[1] *Descriptions des gîtes minerais.*

[2] Gravenhorst, *A Detailed Account of Tinning, etc.* Braunschweig, 1774.

solution of stock from the wine-cask. To-day, for the same purpose, a boiling dilute soda solution is employed.

The object of this study, however, is not to go into the present modern technology of tinning. In principle it has really changed but little when we take away the use of other pickling acids, greases for tinning, mechanical equipment, and electrolytic tinning. The present tinning process may be divided essentially into—

1. Tinning by the blanching process.
2. Fat tinning.
3. Electrolytic tinning (only the contact process and autovolt process), or separation of the tin from tin salt solutions, or by use of tin electrodes, or by aid of the electric current.

For tinning by laying on, there exists a large number of recipes which we assume to be well known.

Blanching Process.—As a rule small metallic objects are tinned by blanching. The well-scrubbed object is brought into boiling tartar solution (5 per cent.) and heated for several hours with the addition of granular tin; the tinned object is then washed with water, rubbed, and dried. Alkali stannates are also frequently used.

Fat tinning for tinned sheet iron is made by three methods: the English, German, and mechanical tinning processes. The first two methods are essentially distinguished by the kind of sheet-iron preparation, and in the mode of tinning large bundles of sheet iron simultaneously. The German method when carefully carried out gives equally good results as the English. The mechanical process hails from Girard. The pickled sheet iron is passed mechanically through the tinning bath. The tinned sheet then passes over rollers in order to strip off excess tin and to render the tinning extremely uniform.

Electrolytic Tinning.—Finally, with regard to electro-tinning, this has made important progress during the last few years, and has a future awaiting it. The *autovolt process* depends on the formation of a feeble electric current by suspending an aluminium basket in an ammoniacal tin salt solution. The object to be tinned is laid in the aluminium basket. The process at its best only gives weak precipitates, and is unsuitable for household utensils. *Electrochemical tinning* depends on the use of a stannous chloride solution with addition of alkali and sodium pyrophosphate as electrolyte and a tin plate as electrode. For electrolytic tinning proper, a whole series of new processes exist, of which the German have hitherto yielded the best results (*Langbein-Pfanhauser's process*).

It would go beyond the scope of this work to enter into the manifold works' methods of the modern tinning industry. We see that the principle of the fat-tinning process, which process has been the one in most frequent use, has scarcely altered in the course of the century. Although the principle has remained the same, the actual technique has made revolutionary progress with respect to furnace construction, working equipment, pickling methods, etc., and may advance still further owing to the effective methods discovered in recent years for recovering in a rational manner the expensive tin from tinned waste and various tinned utensils.

The important part played by the technique of tinning in industry and the household, may be gathered from the following statistics of tin and tinned sheet iron. The world production of tin last year amounted to about 108,000 tons, having a value of about £15,000,000. In the year 1909 there were concerned in the production and consumption of tin:—

	Tin Consumption.	Production.
Germany . .	17,100 tons	8,990 tons
Austria-Hungary	4,070 „	52 „
France . .	8,750 „	—
England . .	17,500 „	16,890 „
United States .	42,800 „	—

England imported 42,392 tons, with an export of 42,092 tons.

The majority of the tin is delivered from the Straits Settlements. Unfortunately, the hitherto easily accessible alluvial bed is almost exhausted, and the cheaper open workings have had to be abandoned for more expensive mining. These facts, combined with the growing demand for tin, explain the extraordinary fluctuations in price which tin has experienced during the last few years. The average annual price for 100 kg. tin amounted in the year

1867	to about	£8 8 0
1870	„	11 12 0
1880	„	8 6 0
1895	„	6 5 0
1900	„	11 12 0
1907	„	16 16 0
1908	„	13 0 0
1909	„	13 2 0

1910 (again rising).[1]

[1] See the collected statistics of the Metallurgical Society A. G., Frankfort-a-M., 1910.

During the past year the price of tin rose repeatedly until it reached £18, 10s.

A spot of growing importance in tin output is Bolivia, whose annual production in 1907 amounted to over 16,400 tons. It is not improbable that in a few years Bolivia will overtake the Straits Settlements in importance.

With regard to tinned sheet iron, England exported alone about 390,000 tons during the past year. In the year 1907 England produced about 700,000 tons of tinned sheet iron in 74 works with 383 rolling mills.

These figures speak best for the high stage of development which the tinning industry has attained up to the present, and strengthens the assumption that the important part played by tin in our historical and technically interesting tinning industry must be maintained for a long time to come.

CHAPTER XII.

THE RECOVERY OF TIN FROM TINNED WASTE.[1]

In Europe, and also in the United States, there are various firms occupied with the recovery of tin by electrolytical means from tinned waste, preserve tins, etc. The majority of such firms exist in Germany, and work up the enormous waste material of the present time. Many methods have been recommended for stripping tin from waste. In some cases acid, in others alkali baths, are employed. The stripping processes in use are therefore classified into acidic and alkaline.

THE ACID PROCESS.

The acid process does not strip the tin sufficiently to allow of the steel being recovered in the Martin furnace. (It is well known that traces of tin unfavourably influence the preparation of steel and sheet steel.) At the most, the sheet-iron waste remaining after the acid tin-stripping process can be employed in the cupola furnace for the production of certain common cast-iron articles. No profitable price, however, can be obtained for the stripped waste, and under the best conditions it can only serve for the production of iron vitriol in works which manufacture acids.[2] About twenty years ago the acid-stripping process held out promise of profit, since the tinned waste contained more tin than at present and at the same time was cheaper to purchase. At that time the tinned waste contained 4 to 5 per cent. tin, and often more. Thanks, however, to the manufacturing progress achieved since that period, the tin content in most tinned waste has sunk to 2–3 per cent. according to the thickness of the sheet.

The most renowned tin recovery plants are those of Dr

[1] See recent literature, "On the Electrolytical Stripping of old Tinned Iron," *Ztg. f. Blechind.*, iii. p. 2674, No. 44, 1910. France annually uses 80 million tins of anchovy, Switzerland over seventy million for the export of condensed milk. The number of preserve tins annually utilised in America is estimated at 700 millions.

[2] Recently the tin-stripping process has been improved (by Goldschmidt and others), so that the stripped iron can be smelted without delay in the Martin furnace.

Goldschmidt at Essen and in North America. Those establishments annually strip about 10,000 tons of tinned sheet-iron waste. The price for the sheet tin from old preserve tins varies from 3·20 to 4 marks.

Smith's Recovery Process.—The oldest acid-recovery process appears to be that of Smith.[1] This process was worked about 1884 to 1885 in both an English and a German works. The latter possessed eight electrolytic baths made of wood, 150 cm. in length, 100 cm. high, and 70 cm. wide. The 5 cm. thick walls were lined inside with a layer of strong caoutchouc. These baths stood upon a platform at a distance of 1 m. from the floor. In the immediate vicinity were two wooden tubs for receiving the waste when stripped. In addition, there were a number of solution, concentration, and crystallisation vats. The waste to be stripped was placed in a large wooden apparatus whose walls were latticed to allow of circulation taking place in the bath. The dimensions of this wooden cooper were 120 cm. long, 85 cm. high, and 30 cm. wide. A certain number of long narrow strips of tinned waste were placed vertically in the mass to play the part of current conductors; the outside ends were soldered together to admit of more easy connection with the main current conductor. These wooden chambers so charged, were connected with the positive pole. The kathodes were constituted of copper plates 120 cm. long, 95 cm. wide, and 1½ mm. thick. The edges of these copper sheets were strengthened by a copper seam. The plates themselves were tinned. The bath was compounded of nine parts water and one part sulphuric acid of 60° Bé. Every vat contains one of the wooden lattice frames described above as anode, and two kathodes which are placed at a distance of 10 cm. from the sides of the wooden frame. Above this wooden vat equipment revolves a traveller which permits of the wooden frame and copper plates being raised or lowered. A mechanical contrivance of levers and eccentrics, which are fixed to the vat and are driven by a steam-engine, imparts a vertical motion to the wooden frame, thus raising it about 5 cm. twice per minute.

At the beginning of the process the tin separated in spongy form, but as soon as a portion of the acid was consumed, the tin settled upon the bath floor in the form of small crystals of tin. After five to six hours the stripped waste is collected and removed to the iron vitriol vat, in which the iron quickly dissolves to form iron sulphate. The electrolyte is very quickly enriched with iron

[1] *Electrochemical Manual*, by H. Becker.

vitriol. In a few weeks the bath is saturated, and then the solution is allowed to run into the iron vitriol vat.

The dynamo employed was a machine of Siemens & Halske driven by an 8-h.p. steam-engine, and yielding 240 ampères at 15 volts E.M.F. Theoretically 4·25 kg. tin per hour should be separated from the eight baths by 240 ampères. Actually only half of the theoretical amount is liberated.

In order to avoid a great loss of chemical products and of tin, the iron baskets holding the stripped waste are immersed in a vat filled with water, after having first been allowed to drain thoroughly into the bath. This water is afterwards used as an addition to the electrolytic liquid, whereby the level of the bath is continually maintained, *i.e.* the bath is kept full.

The nature of the precipitated tin depends on the current strength and the bath temperature. The less spongy the tin is separated, the more readily it fuses. In every case the separated tin must be pressed into blocks or bricks for melting. Indeed, with spongy tin waste a tin paste may be produced for the preparation of tinfoil.

Using a normal current strength, the tinned waste will be completely stripped before the electromotive force has scarcely exceeded $2\frac{1}{2}$ volts (towards the end of the operation) and a light brown colour, due to ferric hydrate, will have commenced to appear.

Chlorine Recovery Process.—Finally, a chemical process for stripping tin may be referred to, which is employed in works engaged in the production of electrolytic chlorine. This is the process first employed at Metikon, in Switzerland. The waste is laid in a large iron cylinder, which is 4 m. high and 1 m. diameter. The waste rests upon a grate forming the floor of the cylinder. The latter communicates with the other cylinder floor by means of a pipe through which the current of chlorine passes. The tin is transformed by the chlorine into tin tetrachloride, which collects in the form of a fuming liquid in a tank placed beneath the cylinder. The tin tetrachloride is transformed into tin dichloride, which finds manifold technical applications.

This short account of the procedure of stripping tin from tinned waste has naturally not by any means exhausted the large number of new and very recent patents and processes for the recovery of tin from waste.

The extraordinary rise in the price of tin during the last ten

years, brought about by the ever-increasing consumption of this metal and its more or less stationary production, has proved a well-timed impetus towards the utilisation of the large amount of tinned waste still remaining. The price of tin has trebled within a few years, and a limit to its maximum market value cannot yet be anticipated.

Gelsthorpe's and Neuhardt's Processes.—Of the other acid processes for stripping tin we may name those of Gelsthorpe [1] and Neuhardt.[2] Gelsthorpe made his experiments on a commercial scale in Manchester, and employed as electrolyte a solution containing 1·25 per cent. hydrochloric acid and a little sulphuric acid. Neuhardt, on the other hand, used as electrolyte a solution of sulphuric acid increased by 11 per cent. ammonium sulphate. This process, however, has never received industrial application.

THE ALKALINE PROCESS.

The alkaline process possesses the great advantage of permitting the use of an iron vat or receiver for the electrolyte, and a basket made of iron wire for holding the tinned waste. This receiver is not only unattacked by alkalies, but the tinned waste stands in better electrical connection with the current conductor. Actually the latticed walls of the basket touch an immense number of places which themselves are connected directly or indirectly with the positive pole. In many works the holders (baskets) for the tinned waste are actually connected directly to the positive pole. This kind of connection is the most efficient, for then the stripping is better, more complete, and quicker.

Mennicke's Process.—H. Mennicke recommends as electrolyte a 10 per cent. solution of caustic soda which is heated to 70° C. According to Mennicke the baths must be prevented from absorbing carbon dioxide from the atmosphere, since sodium carbonate will thereby be produced in the bath, and the presence of this substance not only decreases the conductivity of the bath but also causes tin hydroxide to separate upon the tinned waste, thus preventing the stripping of the tin. Mennicke adds a little sodium chloride (common salt) to his caustic soda baths in order to make it a better conductor. Common salt is cheap, and increases the conductivity better than all other salts.

[1] *Electrochemist and Metallurgist*, December 1901.
[2] *Chemikerzeitung*, 15th January 1902, and D. R.-P. No. 118,368, 1902. Further, *Zeitschrift für Elektrochemie*, vii. 21, 1902.

Borchers' Process.—The famous expert Professor Borchers refers, in his book *Elektrometallurgie*, to a bath composed of a 5 per cent. sodium stannate solution increased by 12 to 15 per cent. of sea salt. According to Borchers, the bath must be evaporated after some time and the tin salts extracted from it.

In a small firm working up two tons per day, one and the same alkaline bath is used for two years without disturbance, except for a filtration from time to time. These filtrations are absolutely necessary for removing from the bath a large amount of impurity proceeding from lacquered or dirty sheet waste. The gradual formation of carbonate in the bath and the enrichment in tin is not very much to be feared.

Through the extensive warping of the basket containing the tinned waste, there is a certain *bath loss*, due to the quantity of liquor which remains adhering to the surface of the waste. A little electrolyte must therefore be continually added in order to maintain the bath at a constant level. Bath loss also arises by evaporation. Accordingly, from real necessity the bath is continually in process of gradual renewal.

CHAPTER XIII.

THE DANGER OF LEAD COMPOUNDS TO INDUSTRY AND THE HOUSEHOLD.[1]

The world consumption of lead is on the increase. While in the year 1880 this only amounted to 300,000 tons, the figure rose from 650,000 tons in 1890, and 820,000 tons in 1900, to 1,090,900 tons in the year 1909.

The average selling price per ton of lead was—

£20	0	0	in 1860,	£10	0	0	in 1894,
17	12	0	„ 1870,	18	6	0	„ 1907.
11	4	0	„ 1885,				

Hand in hand with this extraordinary increased consumption, in which Austria-Hungary takes about 12,000 tons per annum, has the knowledge of the poisonous character of lead compounds raised difficulties in ever-widening circles. Public opinion in civilised countries has endeavoured to bring about protection for all individuals exposed to the possibility of lead poisoning, and during the last few years the fight has been energetically waged against the devastation which lead brings about in manifold ways. Theory and practice have begun to be interested in the question, and although the success hitherto attained is still small, yet partial progress may be claimed.

For judging the merits of the problem it is necessary to consider the effects of lead compounds upon human health. According to Professor Layet, the healthy man possesses about five million red blood-corpuscles, which are of vital importance for digestion and for the renewal of spent energy. Among lead workers, according to Melassez, the number sinks to 3·7 millions after five years, to 2·6 millions after 20, and to 2·2 million after thirty years.

Openly exposed to the dangers of *lead poisoning* are the

[1] This title must not be taken rigidly, since on account of the presence of lead compounds in many ceramic varnishes, there is still a place for a discussion of these in such a work.

painter, house decorator, varnisher, lead smelter, moulder, typographer, potter, and last but not least, the consumer. Of 210 treated for lead diseases at the hospital of Clichy in the year 1898, 159 were painters and decorators, 25 were lead moulders, and 4 were typographers. The average mortality was 17·2 per cent.

Two danger classes may as rule be distinguished, viz.: Class I., Trades and industries working with lead colours, especially white lead (cerussite or $2PbCO_3 \cdot Pb(OH)_2$). Class II., The ceramic industry in general, and pottery in particular.

I have dealt with Class I. in another place.[1] In addition to the basic carbonate must also be noticed:—

Minium[2] (Pb_3O_4), frequently written as of the composition ($2PbO + PbO_2$); Naples yellow, $PbO + Sb_2O_5$; chrome orange, $CrO_4 + Pb + Pb + PbO$; Turner's yellow, $PbCl_2 + 7PbO$, also in the form of oil varnish (siccative), which as a rule is a warm linseed oil triturated with red lead, limonite, manganous borate (about one-third per cent.), zinc oxide and boric acid (about 2 per cent.): all the manipulations connected with it may be followed by after-effects injurious to health.

To-day, no doubt exists that lead white can be replaced with advantage in almost all its applications by the uninjurious zinc oxide (ZnO).[3] In France, where most of the modern proposals for the protection of workers have first been studied, a special commission was appointed which, in the early part of the year 1909, and after five years of exhaustive research in a section of the Pasteur Institute[4] at Paris, reached the conclusive result that lead white may be unconditionally substituted by zinc oxide. The "Société de Médecine publique et de Génie sanitaire" at the end of five years' hard experiment, and after observing and noting the often indecisive results given by experiments with white lead and zinc white at the Pasteur Institute, has established that the materials and paints with both of the products named behave similarly, and that accordingly a conclusion in favour of the one or the other colouring bodies cannot be drawn. Under these

[1] *Neue Freie Presse*, 24th Mar. 1908, and 17th Oct. 1908 (the fight against the common use of lead colours).

[2] Usually known as red lead.

[3] A. Souris, *La Peinture au blanc de Zinc*, Paris, 1902.

[4] I refer to the latest work of Piperau and Vila, chemists at the Paris Pasteur Institute: "The Manufacture of Zinc Sulphide and its use for Painting and Decorative Purposes," *Bulletin de la Société d'Encouragement p. l'Ind. Nat.*, Paris, Nov. 1909. The authors give therein exact directions for the preparation of zinc colours, and come to the conclusion that these can completely replace those of white lead.

circumstances the above-named committee is of opinion that, from the technical standpoint, nothing stands in the way of replacing white lead by zinc white, and that from a hygienic point of view the change is to be desired. Satisfactory results from the replacement of white lead by zinc oxide are in the meantime accumulating, and this fact cannot be met by the answer that white lead paints are forbidden, since the Prussian railway minister had repealed the earlier prohibition.

Owing to the increasing use of zinc oxide, a method deserves to be mentioned for rapidly detecting any impurities present in it. The method is due to Tambon,[1] and depends upon the quick and complete solubility of ZnO in a mixture compounded of equal parts ammonia and of a 20 per cent. solution of ammonium chloride. Tambon termed this solution *triammoniacal solution.* Lead carbonate and barium sulphate are both insoluble in it and sink to the bottom, also metallic zinc particles, zinc sulphide and barium sulphide (proceeding from adulteration by lithopone).

Finally, with regard to the part played by the health-injuring lead compounds in the ceramic industry, especially in the pottery section, it is well known that in spite of the extraordinary development of the earthenware and porcelain industry in an artistic and technical sense, little progress has been made in the chemical modification of lead glazes and colours, quite apart from the customary pottery varnishes, which to-day are still based upon the original primitive procedure. The metallo-ceramic industry, which we may now designate the great enamel industry, stands alone as a praiseworthy exception in this regard, since not even a jot of any lead compound whatever enters into the composition of an enamel. Already Lampadius, Röttger, Wiederhold, Erlenmeyer, and Barreswil in Germany, and Chevalier, Beaude, and Poggiale in France, had been engaged in the investigation of pottery glazes. Erlenmeyer in 1856 examined about 120 pieces of pottery from various centres, and by treating these for several hours with hot dilute acetic acid (1 part of pure acetic acid in 240 parts water) he was able to establish a lead content of 0·15–1 gr. per piece. He reports that lead-free pottery was found from the Bunzlauer, Merseburger, and Kirchenlamitzer districts, but that this was exceptional.

Some potters employed blast-furnace cinder with advantage for

[1] *Bulletin de la Société Chemique*, 1907, p. 823.

glazing purposes, while others used an easily fusible clay. Leibl recommended a glaze of water-glass and lime, others again zinc blende, instead of potter's ore (lead ore) and borax. Lack of knowledge of the chemical composition of the raw materials, of the furnace processes, and of the influence of the higher or lower firing temperature upon the less or greater solubility of the lead glazes in use, account for many of the difficulties met with in the industry. Only by the greater concentration of the industry, by instruction and arrangement of courses, and by the establishment of a central institute for the study of raw materials and glazes, may improvement be brought about.

The lead compounds most frequently used in the ceramic industry are minium or Pb_3O_4, white lead, lead glaze (PbS), and the compound of most general application in the earthenware industry, viz. lead oxide or litharge. For ordinary earthenware lead glance (known as lead ore) is used, this containing from 86 to 91 per cent. Pb. For the preparation of opaque white earthenware and also stoneware glazes, the so-called calcine (also calzine) is used, this being a mixture of PbO and SnO_2 obtained by the gradual melting and oxidising of a lead-tin alloy.

For understanding the dangers connected with the manipulation of lead compounds in the pottery trade, the work of Dr B. Chyzer[1] may be consulted. He estimates the total active workers in the Hungarian industry at 5000, with an average consumption of 420-500,000 kg. of lead oxide annually. The appearance and forms of poisoning are very numerous, beginning with lead colic, gum disease, jaw decay, childbirth prevention, and anæmia, while in some villages there is a universal sterility in marriages of potters. Among the most terrible effects of lead poisoning are included the frequent lead paralysis of the radial nerves, ulnar nerves, hand paralysis, paralysis of the shoulder, muscles, and facial nerves, often blindness, insanity, and epilepsy (by degeneration of the protoplasm).

In 1871 Dr Emil Heubel[2] of Kiew communicated the results of some experiments made upon animals: he found that death in the case of dogs took place in six to seven weeks after a daily dose of 0·2 to 0·3 g. lead. An investigation of the organs was made

[1] Dr B. Chyzer, *Über die im ungar. Tonwarengewerbe vorkommenden Bleivergiftungen*, G. Fischer, Jena, 1908.

[2] Dr E. Heubel, *Pathogenese und Symptome der chron. Bleivergiftungen*, Berlin, 1871.

immediately after death, and the lead contained in 100 parts was for—

Bones	0·025
Kidneys	0·016
Liver	0·015
Spinal marrow	0·008
Brain	0·004
Lungs	0·001

Dragendorff, in his fundamental work, *Die gerichts-chemische Ermittlung von Giften* ("The Legal-chemical Enquiry into Poisons") defines lead as an element, frequently used in industry, which is far from being as stable towards chemical and physical agents as was formerly believed, and which even now people are inclined to accept as safe for application. After dealing with lead dangers in glass works, in the manufacture of sealing-wax (coloured with red lead), and to the painter and printer, he refers to the fact that kitchen water containing air, as well as the moist atmosphere of the kitchen, have lead dissolved in them in appreciable amounts, and moreover, the less carbonates in the water the greater the amount of contained gases. Hard water therefore will attack [1] lead pipes less readily, since it gradually forms a protecting layer of lead carbonate on the inner wall of the pipe. This layer, however, may often be detached, and so become a menace to health.

The use of lead-tin foil as a wrapper for chocolate and other eatables such as tea, has occasioned poisonous symptoms. In this regard aluminium foil has fortunately appeared as a substitute.

Returning to the use of lead compounds in the ceramic industry, we find glazes and the so-called fluxes and colours employed in the earthenware and porcelain manufacture, which, in consequence of their lead content, are able to act injuriously; fortunately an endeavour to seek emancipation from lead compounds is to be noted in this field. When lead oxide is present merely as a flux, it may often be successfully replaced by borax. With regard to the so-called fluxes, which are easily fusible glasses, and together with the

[1] In general, water dissolves more lead the poorer its contents of salts, *i.e.* the softer it is. Rain-water dissolves lead best because it contains almost no fixed salts but oxygen, carbonic acid, and traces of ammoniacal compounds. Leaden gutters are therefore not to be employed where rain-water serves as drinking water. Spring water mostly contains calcium bicarbonate and gypsum. Therefore a firmly adhering layer of lead sulphate, basic carbonate, and also calcium carbonate, soon forms on the inner walls of lead pipes, which, after a short period, protects lead against attack (A. F. Holleman, *Inorganic Chemistry*).

addition of metallic oxides for colouring purposes form the ceramic painting colours, it must, unfortunately, be stated that the majority of these are compounded upon a lead basis, generally from the original recipe of the inventor, *e.g.* those of Salvetat and Brogniart[1] at Sèvres.

1. Rocaille flux:—

Lead oxide, 75 White sand, 25	} lead silicate.

2. Carmine flux:—

Fused borax	55·55
Sand	33·33
Lead oxide	11·12

3. Salvetat flux:—

Lead oxide	60
Sand	15
Crystallised boric acid	25

In decorative enamelling, where for years the attempt has been made to find colours independent even of extremely small quantities of lead for decorative purposes, the following lead-free flux has proved exceptionally trustworthy:—

Sand or quartz	3 parts
Chalk (levigated)	1 part
Calcined borax	3 parts = 5·6 parts of crystallised borax.

This mixture is melted, powdered extremely fine in the porcelain mill, and the corresponding amounts of colouring bodies added.

An example of the composition of an English porcelain glaze, affords information as to the average lead content of such a compound:—

1.

Matt	China stone (Pegmatite)	34
	Borax	34
	Flint (SiO_2)	14
	Chalk	18
Added at the mill.	Matt	70
	China stone	9
	White lead	21

[1] *Traité des arts céramiques.*

2.

	China stone	20
	Borax	35
	Flint	15
	Chalk	18
	China clay (kaolin)	12
Added at the mill.	Matt	65
	Stone	11
	Flint	11
	White lead	13

The colouring bodies most frequently used in the ceramic industry are the so-called *Naples yellow* ($PbSb_2O_6$), which is obtained by the oxidising fusion of 12 parts antimony with the addition of 8 parts red lead and 4 parts tin oxide, or also by the prolonged heating followed by the lixiviation of a mixture of

Tartar emetic	1 part
Lead nitrate	2 parts
Well dried common salt (NaCl)	4 „

Finally, the following analysis of a modern white enamel, such as finds application in present-day enamelling, shows the success which has attended the efforts to be absolutely independent of lead compounds, in contrast to enamel recipes of ten years ago, which contained up to 14 per cent. of lead oxide.

SiO_2	42·6 per cent.
Al_2O_3	11·5 „
CaO	0·3 „
MgO	3·3 „
B_2O_3	6·2 „
Na_2O	12·6 „
K_2O	11·7 „
SnO_2	11·8 „
	100·0 per cent.

I have earlier referred[1] to an easy and rapid qualitative test for the smallest amount of lead in glazes and enamels.

Some years ago well-known scientists were engaged upon the chemical and hygienic investigation of culinary utensils. In 1892 Senatner, in the *Archiv für Hygiene*, stated that in Munich since

[1] *Austrian Chemikerzeitung*, Oct. 15, 1908. Further, see Grünwald, *Theory and Practice of Enamelling on Iron and Steel*, Charles Griffin & Co. Ltd., London, 1909.

1884, two thousand and nine earthenware utensils had been examined for lead by means of acetic acid, and thereof not less than 1307, *i.e.* 67 per cent., had been objected to on account of lead. Professor Dunbar, the well-known Hamburg authority on hygienic matters, tested ninety-nine earthenware pots in 1896, of which fifty-two showed evidence of lead. On the other hand, Professor K. B. Lehmann, the Würzgburg authority on hygiene, was able to claim noteworthy progress for Saxony in this respect. According to a communication by Geheimrat Professor Dr Renk of Dresden, 230 samples from 33 Saxon earthenware utensils were investigated in 1896, and no lead whatever found in the glazes. In a noteworthy work by Professor Dr K. B. Lehmann of the University of Würzburg (*Die Glasuren unserer irdenen Geschirre und der emaillierten Eisengefasze vom Standpunkt der Hygiene*, Hygienische Rundschau, Berlin, August 15, 1902) the results of a research by Lehmann and Dr Baltes were communicated. These investigators found a lead content of 80–180 mg. per 1000 c.c. (boiled for half an hour with 4 per cent. acetic acid). On continued boiling these figures underwent a still further appreciable increase. Dr Thomet of the Würzburg Hygienic Institute established in 1900, that, of a large number of earthenware vessels investigated by him, about one-third could not satisfy the German laws. The experimental results obtained by Professor Lehmann with respect to the lead content of enamelled utensils are important, and from them the following conclusions were drawn:—

"None of the enamel utensils tested, some of which were of a very cheap character, gave more than a trace of lead, so that from the standpoint of the German regulations nothing objectionable could be levied against them."

The German law respecting lead prohibition is certainly too broad and considerate for the extraordinary difficulties encountered in finding all-round substitutes, made exclusively of lead-free materials, for the lead glazes used for earthenware utensils; the proposals put forward by Professor Lehmann might constitute a compromise between the earthenware industry and hygiene. The latter are as follows:—

"Utensils yielding an amount of lead under 5 mg. per litre of 4 per cent. acetic acid, after a boiling period of half an hour, should be classed as unobjectionable."

On the other hand, samples taken from warehouses and market stalls, of which 20 per cent. of the test pieces give a lead content

of over 5 mg. per litre of 4 per cent. acetic acid, should be confiscated and destroyed.

In general, we see that the fight for or against the use of lead preparations, produces opposition of a hygienic or economic character. Whether a higher value should not be finally placed upon the public health than upon the material loss which individual branches of industry would suffer in the event of the hygienic laws being strictly administered, is, in the present position of social development, easy to decide. So long, however, as the existing opposition cannot be completely overcome, a certain compliance on the part of all interested circles will be required.

This short notice on the mode of employment and injurious character of lead compounds in industry generally, and particularly in the ceramic branch, should stimulate all our endeavours towards improving these untenable relations. The best-intentioned precautionary measures, recipes, and regulations are frequently allowed to remain ineffectual owing to the indifference of many workers to all innovations. The evil must be rooted out in all cases where feasible, either by legal prohibition against the use of lead colours, or by scientific research in the ceramic field. The regulations lately published in Austria respecting restrictions and precautionary measures to workers manipulating substances containing lead, must be hailed as noteworthy progress. At the Hygienic Congress held at Berlin from 23rd to 30th September 1907, the Austrian delegate, Teleky, rightly complained about the insufficiency hitherto of the statistics and laws relating to this subject in Austria, while the Hungarian delegate, Toth, referred to the indifference of the workers to the best-intentioned recipes.

The sight of a row of unfortunate lead-poisoned potters or decorators suffices once in a lifetime, and their paralysed hands and feet are a most affecting appeal to us to place all our abilities in the service of the cause, and if necessary to raise our voice against the use of lead compounds regardless of certain industries and trade purposes. The accumulator industry, the construction of apparatus, ammunition, technique, and alloys will ever offer an expanding field for the employment of lead.

CHAPTER XIV.

ON TIN DISEASE, OR TIN PEST.

A REPORT published by Professor Cohen of Utrecht has lately appeared dealing with the quite peculiar phenomenon of *tin pest* or *tin disease*; it will perhaps interest many, for whom the special literature is inaccessible, to learn more details of this disease. In 1901 Professor van't Hoff, to whom physical chemistry owes so much, gave a lecture to the Verein Deutscher Ingenieure at Berlin, wherein he referred to the work of Cohen in this field.

Physical chemistry to-day is fortunately in the position of being able to give us satisfactory and comprehensive information about many phenomena hitherto inexplicable. "The endeavour of physical chemistry is essentially to provide a common meeting ground for chemistry and physics, to connect chemical transformation with the phenomena of physical change, and in particular to find an interpretation for the mutual transformation of the different states of aggregation, *e.g.* from solid to liquid, liquid to gaseous form, etc., in order, after this connection has been established, to be able to apply the simple physical laws governing these phenomena to the more complex conditions of chemical change" (van't Hoff).

Aristotle stated long ago that tin could melt in frosty weather. L. Erdmann in 1851 made a communication to the Academy of Sciences in Leipzig on the transformation of metallic tin into a grey powder, a phenomenon especially noticeable in the case of old organ pipes during a cold winter. In 1869 Fritsche of St Petersburg reported that a consignment of Banka tin in the Customs store had collapsed into dust, a similar case having occurred with a number of tinned uniform buttons in a Russian military store. Fritsche had already accepted the severe cold of the winter 1867–68 as the cause of this occurrence. He proved that tin experiences the same transformation when exposed to an artificially produced cold.

At first small wart-like prominences are formed on the tin and

these continually increase in number until finally the tin object crumbles into a grey powder; by melting this up, metallic tin is again produced. The analysis of the grey tin shows that no chemical change whatever has taken place. Chemically pure Banka tin, of 99·96 per cent. tin content, after being transformed into the grey modification, gave the same chemical composition (Lewald 1870, Rammelsberg 1870, Walz 1872, Petri 1877, Markownikoff 1881, Hjelt 1891, Stockmeier 1893, Schaum 1897).

Cohen entered into a most thorough investigation of this phenomenon, and found that the transformation of metallic tin into the grey modification was connected with a definite low temperature which lay between 20–18° C. This temperature is known as the *transition temperature*. Scientifically the transformation from one modification (system) into another is expressed as: Grey tin, ±20° C. White tin, therefore, can pass into grey below 20° C., and conversely, the white modification is more stable than the grey at temperatures above 20° C. Cohen found that by moistening white tin with an alcoholic pink salt solution (a double salt of stannic chloride and ammonium chloride), the transformation into the grey modification was accelerated in a remarkable way. Grey tin has greater volume and hence lower specific gravity (5·8) than white tin (7·3).

The transformation from white into grey tin proceeds relatively rapidly in the presence of already diseased (grey) tin (when the tin has become inoculated with grey tin or with its nuclei (*keimen*)); on the other hand, this transition takes place extremely slowly at ordinary temperatures, although, as already mentioned, much more quickly below 20° C. At −48° C. the transformation velocity of the white into the grey modification is at a maximum. The transition begins at 18° C. and ceases entirely at −80° C.

In our climate, for the reason stated, tin is found in a metastable condition except on warm summer days, *i.e.* ready to be transformed into grey tin by a lowering of temperature. Fortunately the metastable condition of many elements (*e.g.*, white phosphorus) is fairly permanent. By the transition of white tin into grey a large increase in volume takes place, and in the converse change a contraction. On this property depends the experimental determination of the transition point, which was found to be at 20° C. (dilatometer test). The transformation point (transition point) has been more exactly and satisfactorily determined by Cohen by means of the so-called transformation cell or element.

The element consists of two cylindrical glass vessels a and b, connected with each other by c. In one vessel ordinary tin is placed, and in the other grey tin, there being no mutual contact. A suitable electrolyte is chosen as filling liquid, the best being a solution of pink salt. There now exists electrolytic contact from tin to tin, and by the metallic connection of both modifications through a platinum wire a current is generated. The transformation takes place in such a way that the grey tin increases on the one hand while ordinary tin is consumed on the other, or conversely, this displacement being brought about by migration of the tin ions

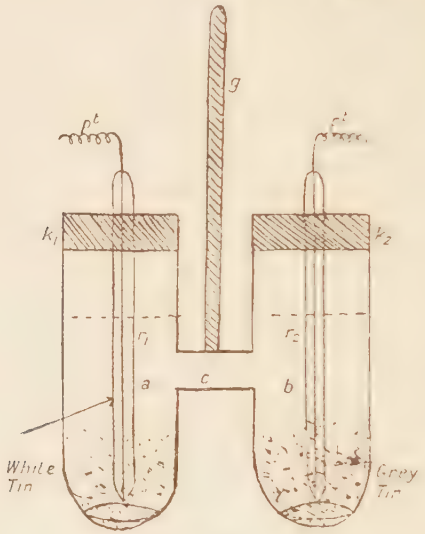

Fig. 5.

in solution. As the temperature of the transformation was gradually lowered it was observed that at 20° C. no electric current (*i.e.* no throw of the galvanometer) passed, so that both tin modifications were in equilibrium at this temperature. Below 20° C. a current flows from r_1 to r_2. At 18° C. a change in the direction of the electric current occurs, and the transition point is then said to lie at 18° C. It must, however, be added that the transition temperature may be altered by change of pressure, a fact expressed in the well-known thermodynamical equation.

Tin pest is often unpleasantly noticeable in museums, *e.g.* in the gradual decay of collections of historical medals (*Museum disease*). A similar decay may also be observed in organ pipes. The best

preventative measure is to maintain the room temperature at a minimum of 20° C. (It is advisable to keep such valuable tin utensils in specially warmed cases, and also to remove carefully any diseased tin; hence organ-pipes, etc., should be frequently inspected.) The name "tin pest" has been given to this interesting phenomenon on account of the peculiarity that by touching sound tin with quite small amounts of grey, the decay of the white tin is brought about or accelerated.

A similar disease unconnected with the transition phenomenon is the so-called *fatigue*. Strongly pressed and in general rolled tin drawn into utensils, undergoes fatigue in consequence of the mechanical manipulation, and frequently falls into a grey powder also. Cohen supposes that this fatigue is occasioned by a transformation taking place of the tetragonal crystals of white tin into the rhombic form which at ordinary temperatures is metastable (*i.e.* it has a condition of stability above a certain temperature). Later researches by Dogens showed that this transformation takes place at 170° C. Ordinary tin crystallises in the tetragonal system and gives not only the grey (amorphous) modification, but also a third variety crystallising in rhombic form. The transition point of the tetragonal into the rhombic form was found to be about 170° C.

The position of this point was established in a very peculiar way, viz. by determining the velocity with which the metal issued at high pressure. For this purpose the solid metal was placed in a cylinder having a hole in the bottom, and the metallic mass passing out in unit time under constant pressure was measured. With metals this mass usually increases with rising temperature, but in the case of tin it sinks very appreciably as the temperature approaches 200° C. This fact is interpreted as a proof of the transformation of tetragonal into rhombic tin. At 200° C. tin is so brittle that it may easily be knocked to powder. Hence the tin in tinned sheet iron must tend to pass over into the tetragonal variety if, for example, it is in the rhombic form as a consequence of rapid cooling (produced by a cold air current, for instance). This assumption, however, has not been verified, since the phenomenon itself takes place in the neighbourhood of the melting-point of tin. According to Cohen, we have in this case to deal with a reverse crystallisation, which is a consequence of the volume increase or the expansion of the crystalline residue already in existence. Rolled tin, tinned sheet iron, tin foil, and in general tin which has been

worked up or is fatigued, is therefore in a metastable form tending to recrystallise.

The same fatigue-disease was also noticed in rolled sheet brass consisting of 62·5 per cent. copper and 37·5 per cent. zinc. Petroleum lamps made from such fatigued sheet brass often showed after some time a kind of rusted and corroded appearance. Also lead in the lead chamber of sulphuric acid manufacture often exhibits a fatigue-disease in the form of warts, and finally crumbles into powder. Quite recently a similar process has been observed in the case of iron.

With regard to the tin pest, it may be further added that the reason why certain brands of Australian and Chinese tin are hardly suitable for tinning purposes becomes obvious when one considers the above-described phenomena; also why twice-melted and very rapidly cooled tin gives a less beautiful oxide than a metal only once melted and gradually cooled.

CHAPTER XV.

THE PROCEDURE IN AN ENAMEL WORKS.

The Covering Process.—The layman imagines the covering of a culinary utensil with enamel, *i.e.* the so-called coating process, to be of an extremely simple character. He supposes that the utensil is dipped into the fluid enamel and then withdrawn as a finished enamelled ware. We in practice, however, do not allow ourselves to be misled by this hazy view of the ignorant layman, but know only too well that the coating process is an important and exacting works' operation. When I say that we know this, I of course speak with due limitation, since, unfortunately, there are individual enamellers who are not as permeated with the great importance of their calling as they ought to be.

In this, as in so many other practical questions, it is advisable for junior chemists, engineers, or future works' managers of an enamel firm, at the beginning of their works' activity to serve an apprenticeship under our usually very able enamelling foremen. In general, the works' director is bound to place value upon such a training, and will derive the greatest possible benefit from having able foremen enamellers reared in the trade. This will be facilitated by putting aside artificial differences of position, by tactful consideration when the foreman is impotent, and by recognition of the great responsibility which often devolves upon him. I gratefully recognise how much useful experience I have acquired from my foremen enamellers, and how much suggestive matter I have gained from intercourse with them, matter which later developed into scientific fact. The foreman observes and operates from practical experience, often being unable to explain appropriately the underlying cause, and he is a grateful pupil for theoretical instruction in the chemical-technical field such as would tend to broaden his outlook. Thus, enough cannot be said for the advantages to be gained by a sincere understanding between foreman and manager. I have never found during my long practical experience

that efficiency suffered thereby, but on the contrary that only good results followed. After this insertion, which to me seemed necessary, I will return to our subject of coating.

The ground coat requires a faultlessly pickled rough ware of not too smooth a surface. Adhering excess of soda (white stains), sand or rusty spots, must immediately be removed by a moderately wet sponge before grounding. For better-class wares it is advisable, therefore, to have stationed by the side of every ground-coater a girl 13–14 years of age, who carefully washes the utensil in this way, carries the coated wares laid upon boards to the drying hearth, and executes the remaining manipulations. The coater is thus spared any loss of time, and correspondingly renders a larger day's production, so that the small expense incurred for the little coater is recouped. At the same time, this is a good preparatory school for the workers, who, in most cases, clandestinely attempt from time to time to coat a piece and thereby, after a year or two, become proficient.

In general, I am opposed to the employment of male coaters except for heavy wares and for those exceeding certain dimensions. The current selling price of the finished ware requires the net cost to be a minimum, and so does not allow for the expense of the labour of a male enamel coater. By the right choice of female coaters, which must be made with patience, it is possible in most cases to create a valuable substitute for male coaters.

Coating by machinery has hitherto not attained any success worthy of the name, since machine work is limited in character, owing to the fact that every kind of handwork is not capable of being replaced in a cheap and simple way by machinery. However, where machine coating is performed, it is often because of the comprehensible aversion of the manager to repudiating the coating machine, which originally had received his warm recommendation. The practical man, however, has delivered judgment upon coating machines. Whether the future will work changes therein of real value must first be seen.

A wider question for the coating process is whether the enamelling should be carried out by hand or with the aid of tongs. Each of these two methods has its adherents, and it would be folly to take sides against either the one or the other. Whether the coating should be made by hand or by tongs depends in general upon local custom. Nothing is harder or more inadvisable, as one knows, than the overthrowing of established manipulation methods

in an enamel works. Either of the two methods can furnish good results with proper management. Doubtless it is more simple to coat without tongs, whereby the often injurious pressure of the tongs upon the wares is avoided.

The *ground enamel* should be powdered into a coarse-grained and fairly diluted condition at the wet mill. The water content of the ground should amount to about 40 per cent., and the grain easily detected by the touch. A ground too finely powdered is bad for covering purposes, and easily gives streaky and uneven parts. Should the utensil have been incompletely washed, solid soda may adhere in places, and, after the grounding of the enamel, may cause stiffening to occur at these places, thereby causing the coating of ground enamel to be too thick in parts. Special attention must be drawn to the need for moistening the flat bottoms of wash basins and plates by means of a sponge, to prevent a too thick layer of ground remaining after coating, since the latter is insufficiently burnt, and after the final firing causes fine diagrammatic cracks. Naturally the ground should not contain too much water. Here, as in all other matters, moderation must be exercised. A useful working principle is to work with a somewhat stiff enamel, and to perform the operations with vigour. Many coaters prefer the converse and objectionable method, from motives of convenience, of working with too great a water content in order to be spared the trouble of giving the necessary rotatory movements during the coating operation.

When the ware is coated with ground, the excess ground enamel must be carefully stripped off the edges; the border is scraped by means of a steel point, or still better, by a sharpened piece of wood, and is an operation which is often not sufficiently appreciated, although indispensable for neat edges. The grounded ware is placed upon pins and dried as quickly as possible upon a hot hearth. Steam drying is to be preferred to any other system. The coater of ground enamel should be stationed between the drying hearth and the firing furnace, in order to avoid unnecessary transport.

As previously mentioned, pulverised fused borax, which is soluble in hot water, is a vehicle worthy of recommendation for ground enamels. Most of the other vehicles are objectionable. Borax has also the advantage of preventing the rusting of the utensils during the drying process.

Sheet-iron utensils are enamelled with either one or two

coatings. Doubtless it is more advisable to provide utensils which have to stand exacting treatment with as thin an enamel coat as possible. The thinner the enamel layer and the thicker the sheet iron, the more durable will be the utensil. In order to attain this object a single coating with a strong covering enamel is often resorted to (*i.e.* containing a high tin-oxide content). Simultaneously, however, an extraordinary economy in wages was anticipated. Experience has not confirmed this expectation. Every enamelling expert knows that in the most favourable cases of single coating, over 30 per cent. of the wares are returned to the works on account of flaws and incrustation. These 30 per cent. after being repaired or re-enamelled, are unfavourably prominent, in the latter instance owing to the difference in colour between their thicker enamel and that of first-class wares. Moreover, in practice it is more advisable and rational to coat with two thin enamels of 5 per cent. tin oxide, than to work with a single white covering of 10–12 per cent. Many experts deceive themselves on this point: the weighty words spoken in favour of the single coat have had a great effect, but by degrees a return has been made to a more correct outlook. Too thick enamel layers should certainly be avoided in the interest of durability. The workers' wages for a single or double coat amount to much the same, since scarcely more than half the number of pieces are produced with a single coat than would be twice covered in the same period. Single coating requires a very consistent enamel, accompanied by a careful and slow rotary movement, in order to produce a fairly thick enamel layer. The double coat makes it possible to work with more dilute enamels, and to observe less precautionary measures. For cheap bazaar wares a single coat is possible, since no value is laid by the customer upon the feeble covering power of the enamel. Wares such as the cloudy grey varieties, which in general are produced with only a single coat, are accordingly very durable.

As a first white coat, a somewhat tough enamel rich in tin oxide is used, which should not be too finely ground (sieve No. 40). Also to the primary white enamel there may be added at the mill up to 40 per cent. of clean white enamel waste, which as far as possible has been previously fused. The blue edges are prepared with advantage at the time of laying the first coating. The drying, in contrast to that of the ground coat, should take place slowly in air. With a single coat the drying and firing upon pins is never advisable.

For a second coat a softer, faultlessly clean enamel of smaller covering power is used. The second white is much more intended to impart lustre and appearance to the ware. It is therefore necessary that the enamel may be somewhat finely powdered.

Clay addition for the first white varies from 8–12 per cent.

Tin oxide	„	„	„	„	6–12	„
Clay	„	second	„	„	5–8	„
Tin oxide	„	„	„	„	4–6	„

Well-ignited magnesium carbonate is recommended as a vehicle, *i.e.* burnt magnesia or magnesia usta, also ammonium carbonate. All other vehicles such as common salt, sal-ammoniac, bitter salt, and even soda, are either objectionable or inadvisable. The effect of the vehicle after addition must be awaited for some minutes.

For certain objects of large dimensions such as plates, baths, and kitchen utensils (enamelled outside), a compressed air-enamelling apparatus has been recently employed with advantage.

Another word upon the question of male or female coaters. The choice of female workers for enamelling purposes is made in a systematic way. Not every worker is suitable for the same task. The same person may be a good cleaner, borderer, etc., but unsuitable for enamelling. The coaters employed must be intelligent, sharp, and nimble girls, who above all things have a passion for cleanliness. Just as a sound mind can only dwell in a sound body, so also can a beautiful ware only be produced in a clean enamel works. The coater is trained to make wrist motions only, the rest of the arm being against the body to allow of as little movement as possible. After some practice beautiful results are obtained, and the worker thereby avoids unnecessary fatigue.

The coating table should be absolutely clean, likewise the floor. Utensils must never be left lying about. Before the day's work is over an inspection must be made as to whether the quantity assigned to the worker has been finished during the day. The coating operation requires the greatest vigilance on the part of the foreman. By the indefatigable superintendence and observation of the processes described, very considerable trade success may be obtained.

CHAPTER XVI.

THE EDUCATIONAL TRAINING OF MANAGERS FOR ENAMEL WORKS, AND THE SCARCITY OF TECHNICAL SCHOOLS FOR THE GERMAN AND AUSTRO-HUNGARIAN ENAMEL INDUSTRY.

UNDER the heading "The Training of Managers for Ceramic Works," there lately appeared an article of considerable value written by Herr Kommerzienrat Max Rössler of Rodach. Stimulated by the latter, I will attempt in what follows to communicate my views on the training required by the future manager of an enamel works, and on the necessity of a technical school for the enamel industry.

Consonant with their character we must distinguish between enamel works in private possession and those under joint-stock companies. Where the enamel works are still in private hands, *i.e.* having only one or two owners, the works' management is generally undertaken by the owners. The latter are frequently the founders also of these works, and being very able practical men, have a natural preference for the commercial side of the undertaking. In such works innovations find as great a difficulty of entrance as drastic reorganisation. Old age has naturally a conservative tendency. Such enamel works are found in countries where only moderate competition, cheap labour, and cheap coal exist, and therefore the industry is observed to flourish now and again in spite of conservative adherence to old works' methods. The matter, however, becomes more difficult when such enamel works are found in industrial centres, where dear labour, coal, and neighbouring modern enamel works (in the form of joint-stock companies) are the rule. In such cases success no longer attends a rigid adherence to the old mode of working, and the co-operation of young up-to-date experts has to be secured.

The owner of an enamel works cannot, unfortunately, in many cases anticipate a worthy successor. Just as a saving generation is often succeeded by a spending one, so in the case of

enamellers. The owner's sons either select other occupations in preference to the not always rosy calling of the enameller, or they spend some agreeable terms at the university, untroubled by examinations of any kind, to return at the end to the paternal enamel works. Consequently the latter constitute the worst type of chief or manager, since they frequently allow themselves to be influenced by every possible variety of servility, and, by their lack of personal experience and knowledge, are exposed to the arbitrariness of their subordinates. Fortunately, besides the cases mentioned, there are also numerous others, where the sons of worthy manufacturers themselves become able followers and earnestly engage in scientific pursuit.

What, then, is the position of the company manager? Unfortunately only the larger works know the necessity of adapting themselves to modern demands, and of calling to their assistance in their undertakings scientifically trained technologists who have had valuable experience. Here also, however, a change for the better is to be recorded, and we find to-day an increasing number of able, academically trained enamel works' managers at the head of many of our leading firms. The time of crude empiricism and secret recipes has finally vanished. Also the enamel industry can no longer ignore the progressive signs of the times, but is compelled to take note of every scientific advance of interest in the chemical and technological field.

What kind of training, therefore, is desirable for an up-to-date works' manager? Certificates of studies in chemistry and technology from a technical college, or better, from a technical university, are an absolute requisite. Fundamental knowledge of inorganic, analytical and physical chemistry, mineralogy, business methods, some experience or practice in gas analysis and in the technology of fuels, in mechanics and elementary machine construction, practice in making simple sketches, some talent for draughtsmanship, a good knowledge of geometry, trigonometry, and general mathematics are indeed indispensable. In addition, commercial knowledge (book-keeping, and a little about the law of commerce and exchange), geography, precepts of administration, shorthand, and especially languages, are extraordinarily valuable. The early acquiring of foreign languages cannot be too strongly recommended. On the one hand, a knowledge of these admits of profitable intercourse with foreign customers, while on the other, the study of foreign technical literature affords the possibility of accumulating experi-

ence. A manager without a thorough knowledge of the language of his workers is an absurdity.

Unfortunately, only a minority of our present works' managers possess the knowledge enumerated above as indispensable for a modern expert. Although the value of practical experience in the works itself far exceeds theoretical knowledge as regards works' management, yet the manager of the future, who previous to his entry into practice has received a theoretical training, will be able to render inestimable service after a few years of practice.

If a university training must be waived as a qualification for the management of small works in the future, nevertheless in the interest of our industry we must express the desire to see such works' managers in possession of a certain specialised theoretical training; and here we arrive at a sore point of the enamel industry which hitherto has received but scant treatment.

There exist mighty combines of influential enamel works which have made it their task to defend commercial interests: they have been justified in a remarkable way, a fact to be greeted with joy for the well-being of our enamel industry. Unfortunately, these protective unions have not hitherto engaged in the purely technical professional problems of the enamel industry, probably because the necessary impulse has been wanting. If, however, this study should serve as an impetus, the neglect may be retrieved. In authoritative circles it seems to have been overlooked that the important enamel industry of to-day possesses no technical schools, testing institution, or professorial chair of any kind. Let us quote some statistics.

While the German ceramic industry, which employs about 60,000 workers, possesses twenty excellent technical institutes with ceramics as a subject, and in addition receives appropriate treatment in the lectures on chemical technology in the majority of technical universities, the German enamel industry, possessing nearly 25,000 workers, has no centre in which future enamel foremen and managers can be trained. The total of 25,000 workers does not include that considerable number which finds occupation indirectly through the enamel industry, such as iron and chemical workers. The annual consumption of sheet iron in the German enamel works is estimated at 90,000 tons; for the preparation of enamels in Germany there are annually consumed about 5 million kg. borax, $\frac{3}{4}$ million kg. tin oxide, several million kg. soda and pickling acids, and thousands of kg. of colouring

metallic oxides. The year's sale of German enamelled wares may at present be taken as about 70 million marks.

In Austria-Hungary a similar state of things prevails. While the ceramic industry of the monarchy, which employs nearly 30,000 workers, possesses about nine excellent technical schools and also a university course, the Austro-Hungarian enamel industry, employing nearly 17,000 workers, has neither technical school nor course of any kind. In other countries there is no improvement. In Germany and Austria-Hungary the enamel industry employs to-day almost half of the number in the ceramic industry proper. What a disproportion in technical schools! It will be seen that our succeeding generation is missing every possibility of training and theoretical development. Also the visiting of a technical university is expensive, and a special training is, at the moment, not in demand.

The technical school ought to make the young man acquainted with the most important theoretical and practical foundations of his later calling, especially with simple qualitative and quantitative analysis, and with the fundamental ideas of inorganic chemistry, mineralogy, and business methods, so far as these touch the subject of enamelling; further, he should learn the technology of the enamel industry, the chemistry of the raw materials, gas analysis, fuel technology, etc. The technical school might at the same time serve as a research institute for the members of a future society to be established for the enamel industry. In present-day practice the case often occurs where the works' manager has arrived indirectly at his responsible post via the office or the store. No obstacle should be placed in the way of an able works' manager receiving promotion to the rank of director as a reward for his energy, industry, and zeal.

On the other hand, however, this circumstance does not exclude the fact that it would be absolutely to the interest of the aspiring enamel industry to establish technical schools for the training of future foremen and works' managers similar to those in existence for the ceramic industry. The position of these schools, equipped with research laboratories and testing workshops, must be as central as possible, in order to make them conveniently accessible to the young people in the enamel industry. In addition, short courses could be established for experts already in practice, as well as for chemists and engineers similarly occupied. Since nearly twenty excellent technical schools are in existence for the benefit

of the German ceramic industry, which latter employs 60,000 workers, it is certainly a modest desire[1] that a provisional technical school be erected for the German enamel industry employing nearly 25,000 workers. Eventually such a school could be linked up with an already existing school for ceramics. The same applies to Austria-Hungary. It is obvious that instruction of a commercial character should be given in these desirable schools within restricted limits.

Every industry has its successful managers. If the flourishing machine and chemical industries of Germany excite the admiration of the whole world, and if the productions of the ceramic industry find their way into every land without fear of competition, credit must be given to those able technologists, chemists, and ceramic experts who have been trained in excellent university faculties and in intermediate schools.

The enamel industry, also, will follow the example of all the great specialised industries, and sooner or later must have special schools and research institutes erected for its promotion.

[1] Much would also be achieved by the organisation of university chairs for enamel technology and the chemistry of enamels, in the metallurgical section of our technical universities.

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